
WATER RESOURCES AND WATER QUALITY

Concerns about the quality and availability of water resources have a long history. The constant attention accorded this subject reflects man's dependence on water for personal use, farming needs, and industrial processes. Today, the pollution of inland and marine waters is recognized as a serious and growing problem. The quality of potable water and the threat of waterborne diseases (for example, cholera and typhoid) are critical public health issues in many developing countries. Flooding has become a recurrent event in many parts of the world, while in some countries water diversion schemes have come under attack for causing damage to ecosystems and precipitating changes in local climates.

Chapter 5 begins by considering how monitoring procedures vary, depending on the type of water body being monitored. The determinants and characteristics of each submedium are distinct and require equally distinctive monitoring strategies. With so many options, generalizations become difficult or even misleading. This chapter therefore begins with a discussion of general issues and then goes on to describe the monitoring systems for three submedia-rivers, lakes, and groundwater-along with

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several related features such as sampling frequencies, laboratory techniques, and measures for quality control. A number of parameters that are usually included in any monitoring program are examined in the section Water Parameters. Methods of measuring effluent discharges are considered in the section Estimating Water Discharges, and the main issues to be addressed when monitoring water quantity are outlined in the section Water Quantity and Uses.

Statistical Relationships

Most countries collect statistics on effluent loads (discharges into receiving water bodies), water quality, and water quantity. The significance of these topics is obvious, but the organization and interpretation of the data are by no means straightforward. Problems arise because of several unique characteristics of this medium. First, water, unlike air, is a medium consisting of several submedia: watercourses (ranging from brooks and streams to large rivers), lakes, and groundwater resources such as aquifers and salt-water bodies. Each submedium has its own particular set of attributes that must be taken into account in the statistical process. Moreover, water quality varies not only between submedia but also within a particular water body. The water quality of a river, for example, changes over its course due to natural circumstances (for example, differences in the river bedrock or inflows from tributaries) and human-caused factors such as municipal and industrial discharges or the construction of physical barriers such as levies or dams.

Second, the statistics for the three topics are closely interrelated or interdependent. This interdependence makes it difficult to interpret results and to identify lines of causation. The relationship between water quality and the discharge of effluents is an obvious one. When a waterway's natural capacity to transform and recycle discharges is exceeded, its water quality deteriorates. Discharges into the water depend mainly on conditions in the industry sector—that is, on determinants such as

production technologies, market demand, and product mix. Quality, however, is determined not only by discharges but also by the hydrological regime. The natural factors making up this regime include the geological characteristics of the subsoil, soil properties, and meteorological determinants (for example, precipitation, temperature, and radiation during different seasons of the year). Policy makers would like to know precisely how various economic activities alter water quality, but, in practice, it is almost impossible to distinguish these effects from those of natural factors.

The interrelationships between water quality and quantity create similar problems. The simple fact that a small body of water is more easily polluted than a large one is an example. Water quality may be a function of the volume of effluents discharged, but it also depends, indirectly, on factors relating to quantity—for example, hydrological conditions and the volume of water used for irrigation, industrial purposes, and other needs. Policy makers cannot be sure that their efforts to control the discharge of effluents will yield the desired results unless they have corresponding data on precipitation, evaporation, and water usage. Furthermore, all this information must be available for each body of water being monitored.

Third, the statistical approaches employed in each of the three fields are not fully compatible. Methods for recording discharges and monitoring water quality are well established, but no clear connection between the two approaches exists. The main reason for this discontinuity has to do with the widely different sets of determinants noted above. The subject of water quantity poses its own set of problems. No comprehensive system is available to link data on surface water and groundwater with related issues such as water usage and hydrological conditions. To deal with this multiple set of concerns, statisticians employ an accounting approach that differs fundamentally from the methods used to track the discharge of effluents or monitor water quality.

Monitoring the Quality of Surface Water

Programs to monitor water quality are generally intended to serve at least two purposes. One is rooted in the laws, regulatory directives, and water-quality standards of the country. The results of a monitoring exercise should enable public officials to judge quality in relation to legal standards, assess the environmental state of the country's water system, and identify key trends. A second purpose is to supply both government officials and the general public with findings that can be used to develop and implement measures to improve water quality.

To meet the information needs of policy makers, two types of networks may be required:

- (i) An extensive network generally consists of numerous sampling sites, comparatively few annual samples, the analysis of just a few variables, and one or only a few years of sampling history.
- (ii) An intensive network consists of sampling sites providing data for detailed investigation, numerous annual samples or the measurement of many variables, and several years of observations.

Both extensive and intensive components are found in some monitoring programs. In such a case, one subnetwork consists of a number of sampling stations where data is collected for only a few parameters. A second, intensive subnetwork makes use of a few stations with frequent samples being collected for several variables.

The time horizon associated with monitoring activities is another distinctive feature. Most programs will have a legal justification and are therefore long-term in character. Their emphasis may change as new laws are passed or when new methods of water quality management are perfected, but the need to measure water quality will continue. Long-term programs, however, must sometimes be supplemented by special

surveys or other short-term projects. For example, it may be desirable to survey certain water bodies on an occasional basis or to conduct one-time surveys of a particular pollution problem such as the occurrence of a pesticide in surface waters.

The topography, geology, and hydrology of the area to be monitored should also be taken into account. In the case of a river monitoring system, for example, the designers must be sure to locate stations at sites that are representative of all hydrological features such as zones of turbulent flow, zones of normal flow, and confluences. The land uses of the surrounding catchment area also affect water quality. The water quality of a river will vary, depending on whether the catchment area consists primarily of forest or agricultural land.

Finally, sampling frequency depends on various determinants such as the monitoring objectives, the statistical variation of the parameters, the concentration of pollutants, and the availability of financial and human resources. In the absence of any background data on the parameters, a preliminary decision about sampling frequency can be made on the basis of some knowledge of local conditions. When a sufficient amount of data has been collected, the frequency can be modified as required. Statistical methods can also be employed to determine frequency, provided that some data on water quality at a given location is already available and is normally distributed. In that case, the number of samples that must be collected during a given period of time (day, week, month, year, or season) so as to obtain an average value for a particular parameter can be calculated using the following equation:

$$N \geq \left(\frac{ts}{U} \right)^2$$

Where N = the number of samples to be taken
 t = student-t statistic for a given confidence level
 s = the standard deviation
 U = acceptable level of uncertainty

River monitoring networks. Many countries operate programs to monitor river water. Major rivers are typically singled out for attention, although the more elaborate networks may include some small rivers and streams. In addition, there are various international programs supported by organizations such as OECD and the EU, and the Global Environmental Monitoring System (GEMS) operated jointly by WHO and UNEP.

National river monitoring networks are generally intended to serve one or more of the following purposes:

- (i) provide a general characterization of rivers in the country;
- (ii) monitor the water quality of rivers draining specific areas (for instance, reference sites in forested or uncultivated areas) or leaching substances from agricultural watersheds; and
- (iii) supply the data needed to estimate riverine loading from land into coastal areas, or the loading of transboundary rivers from one country to a neighboring country.

Many networks serve multiple purposes. For example, data obtained via monitoring may be used to make a general characterization of river water quality and to estimate the nutrient loading of coastal areas. Often, a network will consist of two or more sub-networks, with a few intensive sampling sites on major rivers and numerous basic sampling sites located at less important tributaries and river reaches.

Decisions regarding the number of sampling sites and their locations depend, in part, on the program's objectives and costs. However, other factors must also be addressed if statisticians wish to develop indicators that are representative of conditions over long stretches of a river or large regions of a country. One of these factors is the areal density of the network. In developed countries with large river systems, a comprehensive network may consist of several hundred sites, but in many countries the number is far less. The density of sampling sites can range from 1 site per 10,000 square kilometers to more than 5 sites per 1,000

square kilometers, although 1-2 sites for every 2,000 square kilometers is typical. Another determinant is the population of the area under study. The density of sampling sites in relation to population varies from 2 to 500 sites per million inhabitants. The length of the river itself is relevant, with each sampling site representing from 6 to 6,000 kilometers of river. Most sampling sites will be located downstream of specific sources of effluent discharge. However, one or more monitoring stations should be situated upstream of major discharge points to determine the pollutant loads from an industrial or municipal discharge. Finally, the primary data should be accompanied by a description of the location where it was gathered (for example, information on the catchment area).

Networks created to monitor water quality and the loading from specific catchments may encompass up to 20 small streams and require detailed studies of both water quality and the characteristics of the catchment (for example, land use or soil type). A different configuration is appropriate when the purpose is to estimate the riverine loading of contaminants from land to sea, or in a transboundary river. Generally, these networks consist of sampling sites located at downstream points in all major river systems. The geography of the country also influences the design. Countries that have a long coastline compared to their area tend to have a large number of relatively small river systems. Consequently, numerous sites are needed to estimate loads to coastal areas. A much smaller number is required in countries dominated by a few large river systems.

Lake monitoring networks. Programs to monitor the water quality of lakes are less common than those for river-based systems. Attention generally focuses on the largest lakes or those known to have specific problems such as acidification or eutrophication.²⁹ In many developed countries, local governments operate lake-monitoring programs and methods are not standardized at the national level.

²⁹ Eutrophication is the enrichment of water by nutrients (especially nitrogen and phosphorus compounds, and also organic matter). The result is an accelerated growth of algae and higher forms of plant life, which upset the balance of organisms present in the water and jeopardize the quality of the water.

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Lake-monitoring programs may either use intensive sampling procedures or rely predominantly on surveys. A program based on intensive methods will have a sampling frequency of several times per year and cover only a small number of lakes. The survey-type approach focuses on a large number of lakes that are sampled over long intervals (every five years, for example). The lakes to be surveyed are either determined subjectively or identified by statistical criteria. Sometimes, a survey program will be supplemented by a series of intensive annual studies of a relatively few lakes.

The purpose of a survey-type approach is to determine the general environmental state of lakes and, perhaps, to identify specific problems that will be followed up by a more detailed study. Intensive programs are necessary to determine the exact environmental state of a lake, but they are relatively costly due to the higher level of detail sought. Other issues that intensive programs may address include the chemical water quality, biological status, seasonal effects, level of nutrients, acidification, toxicity, and eutrophication.

Monitoring the quality of groundwater. Two important characteristics distinguish groundwater from surface water and should be borne in mind when designing a monitoring network. These are:

- (i) the slow movement in groundwater with relatively large residence times; and,
- (ii) the considerable degree of physical and chemical interdependence between groundwater and the material of an aquifer.

Most networks are intended to identify trends in water quality and to serve as a general means of surveillance. Other possible objectives are to detect the intrusion of seawater in countries with long coastlines, evaluate the impact of airborne pollutants, or comply with legal requirements governing the quality of drinking water.

Three general types of networks for monitoring the quality of groundwater are in use: basic, specific, or temporary networks. A basic

network is intended to provide general information about the quality of groundwater. Ideally, it will cover the entire country, and monitoring operations will be of a permanent nature. Reference stations providing background information on the natural quality of the groundwater are an integral part of a basic network. The information gathered via this network forms the basis for evaluating future trends in quality and for specific investigations of hydro-geological conditions. The design of a basic network will generally take into account the following principles:

- (i) Stations could be placed in a square net or some other geometrical pattern with a fixed distance between them.
- (ii) Stations should be placed in the main aquifers.
- (iii) Stations should also be located in other important aquifers in the area that are selected to ensure that the results are representative.
- (iv) Reference stations providing background information should be established outside areas affected by direct human activities such as groundwater pumping and other anthropogenic changes.

Specific networks are meant to monitor selected areas or specific kinds of pollutants emitted from point sources. Such a network can function independently, or it can be an extension of the basic network. In the latter case, it will have to fulfill the need for data in areas between different sites of effluent discharge (point sources) in the larger basic network. A specific network can have a permanent character, but it may also be in operation only while information is needed at the particular location. For example, around landfills a specific network may be operated as long as the landfill is active and for a specified period after the landfill is closed.

Temporary networks are established to collect data for particular projects. The network will be operational during the project period, after

which it is closed. Eventually, some stations may be transferred to a basic or specific network. A temporary network will usually be more dense than a basic or specific network and the data obtained on groundwater quality will be used in a variety of studies conducted on the area.

Whatever the type of network, there appears to be no generally accepted guidelines for the minimum density of monitoring sites. However, some of the factors that govern decisions about location and density include the following:

- (i) size of the area to be monitored
- (ii) geological and hydrogeological complexities
- (iii) sizes of the main aquifers
- (iv) land use in the area
- (v) ease of access to the area

Possible sources of groundwater contamination include diffuse sources from the atmosphere; diffuse sources from land use (primarily farming); and point sources such as landfills, contaminated sites, and leaking sewer systems. The density of monitoring stations will be higher when point sources rather than diffuse sources are the main concern. Areas known to have a high rate of infiltration also need to be monitored intensively. A lower density is acceptable in areas with sparse populations, minimal amounts of arable land, and no serious point sources of contamination. Finally, the designers of any network should attempt to monitor all major aquifers if financial and human resources permit.

Sampling frequencies. The foregoing description of each monitoring system noted certain differences in sampling frequencies. This issue is an extremely important one and deserves more attention. Both the quality of the data and the overall cost of the monitoring exercise depend crucially on the frequency of sampling, and more details are provided here.

The sampling frequencies recommended for GEMS/Water project stations are summarized in Table 5.1. Three types of monitoring sites or stations are identified. Baseline sites are required to determine the generality of runoff behavior in the region or country. In the case of river monitoring, at least some stations should be located in natural catchments where little or no human activity exists and where most of the catchment is natural landscape. Usually, a majority of the stations will be trend sites. In a river monitoring system, these stations would be situated downstream of major polluters. Flux sites are generally placed where rivers discharge into the sea, where they cross national boundaries, or where there is an interchange between surface water and groundwater.

The number of minimum and optimum samples varies with the submedia. Rivers, depending on their size and flow regime, are frequently sampled over the year. The quality of groundwater aquifers is more stable and usually requires fewer samples; no specific recommendations are made. Sampling is required less often in lakes than in rivers, but data may need to be collected more frequently for specific causes such as eutrophication. In the case of specific issues such as river flux or eutrophication, the required number of samples in a given period of time is generally greater.

In countries where seasonal variations are great, more frequent samples will need to be collected. To monitor the quality of surface water, the following recommendations are offered in the GEMS project:

- (i) Weekly samples should be collected for one year.
- (ii) Daily samples may be collected on seven consecutive days, once in each quarter.
- (iii) Hourly samples may be collected over a 24-hour period, once in each quarter, and every four hours for a period of seven consecutive days in each quarter.

In the case of groundwater, samples may be collected at weekly or fortnightly intervals for some time so as to establish the water

Table 5.1: Recommended Annual Sampling Frequencies for GEMS/Water Quality Stations

Station Type	Rivers/Streams	Type of Water Body Lakes/ Reservoirs	Groundwater
Baseline	Minimum: 4 samples, including high and low water stages Optimum: 24 samples (i.e., fortnightly sampling and weekly sampling for total suspended solids)	Minimum: 1 sample at turnover (sampling at lake outlet) Optimum: 1 sample at turnover and 1 vertical profile at end of stratification period	
Trend	Minimum: 12 samples for a large drainage area (ca 100,000 kilometers) Maximum: 24 samples for small drainage area (ca 10,000 square kilometers)	Eutrophication issue: 12 samples, including twice monthly during summer Other issues: Minimum: 1 sample at turnover Maximum: 2 samples (one at turnover, and one at maximum thermal stratification)	Minimum: 1 sample for large, stable aquifers Maximum: 4 samples for small alluvial aquifers Karstic aquifers: same as rivers

Table 5.1: Recommended Annual Sampling Frequencies for GEMS/Water Quality Stations (continued)

Station Type	Rivers/Streams	Type of Water Body Lakes/ Reservoirs	Groundwater
Global river flux	<p>Large basins (>200,000 square kilometers):^a 6 samples for some particulate metals^b 12 samples for all other variables</p> <p>Small basins (<200,000 square kilometers):^a 24 samples for basic monitoring variables^c 12 samples for expanded nutrients, organic contaminants, and some expanded metal monitoring^d 6 samples for some particulate analysis^b</p>		

^a For global river flux stations, a continuous record of water discharge and weekly sampling for total suspended solids is recommended.

^b For particulate arsenic, cadmium, chromium, copper, lead, mercury, selenium, and zinc.

^c For temperature, pH, electrical conductivity, dissolved oxygen, calcium, magnesium, sodium, potassium, chloride, sulfate, alkalinity, nitrate plus nitrite, total phosphorus filtered and unfiltered, silica, chlorophyll a, organic carbon dissolved and particulate, organic nitrogen dissolved and particulate.

^d For dissolved and particulate fractions of aluminum, iron and manganese; and for dissolved arsenic, cadmium, chromium, copper, lead, mercury, selenium, and zinc.

Source: WHO (1992).

characteristics at a monitoring station. Afterwards, samples may be collected less frequently over the year.

Monitoring stations and equipment. A wide range of terminology is used to describe the various types of monitoring stations. Usually, the stations are identified by the information provided. Some of the more important types of stations follow:

- (i) benchmark or reference stations aimed at characterizing catchments that are undisturbed, as far as possible, by man;
- (ii) boundary stations intended to describe fluxes either between legal boundaries or between submedia (from a river to a lake or ocean, or from a surface stream to groundwater);
- (iii) impact stations used to monitor well-defined pollution sources; and
- (iv) representative stations that can be used to provide summary information for a large area, usually with long records.³⁰

Either automatic or manual equipment can be used. In the case of automatic equipment, the monitoring devices include probes immersed in a water body and measurement occurs in situ. These devices employ a self-contained, battery-operated instrument that can be used up to 300 meters below water level. With automatic equipment, the task of laboratory analysis is greatly simplified. The costs, however, are substantial compared with those for the manual approach and operation requires special skills. If manual methods of monitoring are used, additional sampling apparatus and reagents are needed, depending on the parameters to be analyzed.

³⁰ Other types of stations are (i) stationary stations providing data intended to fulfil legal commitments; (ii) operational stations set up to manage day-to-day issues of water quality by local, regional, or national agencies; and (iii) research stations operated as part of specific scientific projects.

The analytical methods used with automatic water quality monitors (or on-line instruments) closely parallel those used in the laboratory. The main difference between laboratory instrumentation and on-line instrumentation is in the robustness of construction of the equipment and the availability of auxiliary systems in automatic monitors to allow for sample preparation, instruments/sample line cleaning, and instrument calibration.

Ideally, an automatic monitor will use low-cost, non-invasive measurement techniques, produce highly accurate results, and require little or no maintenance. In reality, a more realistic goal is to obtain results of acceptable accuracy at modest costs, with a service requirement not greater than once per week. The main features of an automatic water monitor that would be required to achieve this goal are as follows:

- (i) appropriate location of sampling sites;
- (ii) strong construction designed for a specific purpose (including adequate physical protection provided by the instrument housing) and robustness of the operational methodology;
- (iii) tolerance for extremes of temperature likely to be encountered;
- (iv) resistance to the ingress of dust and water;
- (v) tolerance for electromagnetic fields, electrical transients, and power supply disturbances;
- (vi) minimum supervision and maintenance requirements; and
- (vii) a design that allows for easy access and repair.

Monitoring applications require predictable, long-term analytical performance in terms of accuracy and reproducibility to ensure data

comparability. Attributes such as a fast response time and high sample-throughput rates are normally of less importance. The selection of a monitoring instrument (which is governed by the method of analysis) should take into account the use for which the data is intended. For example, instruments based on well-documented colorimetric methods can produce data of predictable and consistent quality.³¹ Finally, the degree of complexity inherent in any installation depends on both the measurement technique and the nature of the sample. Most parameters can be measured in a straightforward manner, but a few, such as a phenol or a treated or partially treated waste effluent, require a high level of operator input.

Sampling and laboratory techniques. Technicians should be familiar with some basic principles and techniques of sampling regardless of whether the system is manual or automated. The spatial and temporal variability of the parameters are two of the more prominent factors to be considered in the case of river monitoring. The dilution and dispersion of pollutants are subject to temporal variability owing to seasonal changes and related climatic effects. Spatial variability of pollutants, on the other hand, is evidenced by the extent to which pollutants are mixed with the water. In a typical river body, spatial variation of pollutants is governed by the width and depth of the river and water velocity. Thus, for a shallow river where the flow is low, samples are collected from an average depth in the middle of the river, whereas for a deep river with a high flow, samples need to be collected at various depths.

A variety of different types of samples may be required, depending on the purpose and availability of resources. For instance, samples may be collected at a particular time from a single location, or from various locations over a period of time. The different types of sampling methods used are described below.

A grab or spot sample may be "discrete" (that is, the sample is collected at a specific location, depth, and time) or "depth-integrated"

³¹ These instruments sometimes have a long response time. Such delays can be inherent in the chemistry involved. Instruments based on such methods may not be ideal for control applications requiring a fast response, but are generally well suited to monitoring applications.

(the sample is collected over the entire depth of the water column at a specific location and time). Obviously, grab or spot samples can only represent the composition at the time and location when collection occurs. The grab method is useful for the following purposes:

- (i) characterize water quality at a particular time and location,
- (ii) provide information regarding the minimum and maximum measurements of a parameter,
- (iii) allow collection of variable sample volumes,
- (iv) monitor a stream that does not flow continuously,
- (v) analyze parameters that are likely to change, and
- (vi) establish a history of water quality over relatively short time intervals.

A composite sample (also known as a time composite) is a mixture of grab samples of equal or weighted volume, all collected at the same location at different points in time. Composite samples are useful for assessing the average concentration/load of pollutants (for example, assessing the average load of a particular pollutant in an effluent treatment plant). This method of sampling reduces the time and effort that would otherwise be required to obtain several grab samples and then compute the average from a range of data. Normally, a composite sample is collected over a 24-hour period, but it can be taken for different shifts or cycles of any particular operation.

Integrated (or composite) samples are mixtures of grab samples collected from different points simultaneously. These are useful for monitoring the water quality of rivers or other water bodies when variations in width or depth are significant. Integrated samples provide an estimate of average water quality at the time of sampling. Special equipment is required to collect samples at particular depths without

contaminating the overlying layer of water. The method is relatively complicated since it requires a knowledge of both the water flow and the composition of various layers.

Usually, more than one laboratory analytical method is available for almost all water quality parameters. The most appropriate technique depends on the concentration of the pollutant in the sample, the degree of precision or accuracy required, the complexity of the analysis, and the possibility of interference from other chemicals. In addition, technicians should be aware that the samples obtained for some parameters will be "nonconservative," meaning that values can change in the time between collection and analysis in the laboratory. In such a case, safeguards are needed to ensure that the sample is immediately stabilized before dispatching it for laboratory analysis.

Elements of quality control.³² The selection of an appropriate format for data storage is a simple, but critically important step to ensure data quality. The format should provide ready access to all relevant sample details such as date and time of sampling and grid references. It should allow easy examination of the data for errors, and facilitate the rearrangement of the data into subsets as required.³³ Second, it is important that all associated information be recorded alongside the actual sample value. This information is needed not only for the purposes of the monitoring scheme, but also to help validate the data. Third, a common format for data transfer should be used by all suppliers and users so that no errors are introduced when the information is transferred from one group to another.

The simplest check for errors in data entry is to identify values falling outside an expected range. These outliers can be verified, corrected, or discarded as appropriate. However, data should only be discarded when it is clear that an error exists. Outliers occurring as a result of random variation are valid and their exclusion will bias

³² In addition to the procedures described here, the reader should refer to the discussion of quality control in Chapter 3 which, contains additional material of a general nature that is relevant.

³³ A number of commercial database systems can serve these purposes.

results. Methods for checking data in relation to the expected range include the following:

- (i) When checking the sample data gathered for the parameters, one way to identify errors is to flag all observations greater than three standard deviations from the mean of the parameter. The validity of the flagged data can then be verified with the supplier or source.
- (ii) A similar approach is to flag the highest and lowest X percent of the data for a determinant (where X percent is some suitably small value such as 1 percent).
- (iii) The information recorded for fields other than parameters such as grid references may also include errors and should be checked. Dates before or after the start or finish of a monitoring exercise are obviously wrong. Grid references that do not correspond to the appropriate water body are also incorrect. In some cases, other variables can be used for cross-checking. For example, dates that are not synchronized with sample codes would mean that either the codes or the dates are wrong.

Another method of quality checking is to use a statistical quality assurance scheme, in a way similar to analytical quality control. A number of data records are selected at random (with replacement) and checked for mistakes. The proportion of errors in the database is estimated from the proportion of errors in the randomly selected records, and a confidence interval for the proportion is set. Quality standards are being met if the true proportion of errors is below the prescribed level, estimated at a certain level of confidence.

Water Parameters

A large number of parameters may be included in any program to monitor water quality, and several are considered in this section. Physical parameters are discussed first, followed by chemical and biological parameters. In each case, the reasons for monitoring are summarized, the typical sampling frequencies are noted, and the recommended testing procedures and apparatus are described.

pH and temperature. pH is defined as the negative logarithm of the hydrogen ion concentration, that is, $\log[H^+]$ in water. Pure water is ionized to a very small extent into its basic components, H^+ and OH^- , and at equilibrium, the product of concentrations of H^+ and OH^- is constant $- 10^{-14}$. Thus

$$[H^+] + [OH^-] = 10^{-14}$$

The above equation is easier to express in logarithmic form, as follows:

$$\log[H^+] + \log[OH^-] = -14$$

Changing all terms to negative

$$-\log[H^+] - \log[OH^-] = -(-14) = 14$$

Thus, as defined earlier,

$$pH + pOH = 14$$

It is clear from this equation that as pH increases, the pOH decreases and vice versa. Water with a pH level of less than 7 (when the concentration of H^+ ions is greater than that of OH^- ions) is considered acidic. On the other hand, when the pH is above 7 (when the concentration of OH^- ions is greater than that of H^+ ions), the water is considered alkaline.

A number of processes, such as water softening, precipitation, and corrosion control, are dependent on pH. Measuring the pH is therefore important when monitoring water quality. Measurement is a relatively simple process, which can be accomplished with the help of a commercially available pH electrode (probe). Most commercial pH probes come with a temperature probe. Temperature is also monitored every time pH is monitored. In case the pH probe does not have a temperature probe, the temperature can be measured by a good quality mercury thermometer having markings for 0.1°C.

The commercial probe that is generally used consists of a glass tube (electrode) and a display that indicates the pH. It is important that the probe be calibrated, using freshly prepared standard solutions of known pH. Once calibrated, the probe is lowered into a sample solution or directly in a water body in the field and the pH is read on the display of the unit. The probe must be kept in the sample until it displays a steady reading. Because pH is affected by temperature, it is important to report the temperature at which the pH is measured.

Temperature is of more general significance in the monitoring process because it affects several chemical and biochemical reactions that occur in nature as well as in water and wastewater treatment plants. Temperature also affects precipitation and the dissolution of pollutants in water. Finally, the discharge of effluents at high temperatures can alter the aquatic ecology of the receiving waters. Measuring water temperature is therefore critical when monitoring water quality.

Solids. The term "solids" refers to the matter suspended or dissolved in water. "Total solids" are the residual materials left in a vessel or plate after all the water in a sample has been evaporated by drying in an oven at a specified temperature. Total solids include total suspended solids (TSS)-that is, the material left on the filter when the water sample is filtered-as well as total dissolved solids (TDS), which is the material that passes through the filter.

The presence of suspended solids in natural waters may be undesirable for various reasons. It can increase the turbidity of the water, which affects light penetration. This characteristic, in turn, affects the biological life in the water body. It may also be aesthetically undesirable

for such purposes as bathing and recreation. The presence of dissolved solids can alter the taste of water and, at high concentrations, can affect the physiology of the consumer. Waters with high dissolved solids content are unsuitable for industrial applications or for irrigation. The analysis of solids is also important for determining the efficiency and control of physicochemical and biological wastewater treatment processes, as well as for assessing regulatory compliance.

Under normal conditions, the initial frequency of sampling will vary from one submedium to another. In rivers, sampling may initially be once every two weeks; for lakes the frequency would be once every two months, and for groundwater, once every three months. After sufficient experience has been gained, statistical analysis of the data can determine if these sampling frequencies should be altered.

The testing procedures for determining the concentration of solids in a water sample requires that a known volume of water be evaporated and the weight of the residual solids measured. Total solids are measured by placing a known volume of a well-mixed sample in a preweighed dish and dried to constant weight in an oven at 103-105°C. To determine TDS, a known volume of well-mixed sample is filtered through a standard glass fiber filter and the filtrate is evaporated to dryness in a preweighed dish. The calculation for the TDS is similar to that for total solids.

TSS are determined by calculating the weight of the solids on the filter. For this, the filter paper is weighed before a known volume of a sample is filtered through the paper. After filtration, the filter paper along with the residue is dried in an oven to a constant weight at 103-105°C, and then the filter paper is weighed again. The difference in the two weights gives the weight of the residue retained on the filter paper.

Total solids can be calculated as follows:

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume (mL)}}$$

where A = weight of dried residue + dish in mg

B = weight of dish in mg (determined prior to placing the sample in the dish)

TDS can be calculated as follows:

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume (mL)}}$$

where A = weight of dried residue + dish in mg
 B = weight of dish in mg (determined prior to placing the sample in the dish)

TSS can be calculated as follows:

$$\text{mg total suspended solids/L} = \frac{(A - B) \times 1000}{\text{sample volume (mL)}}$$

where A = weight of dried residue + filter in mg
 B = weight of filter in mg (determined prior to filtering the sample)

The apparatus required for measuring solids includes evaporating dishes of 100 mL capacity made of porcelain, high-silica glass, or platinum; a drying oven for operation at 103-105°C; a muffle furnace for operation at 550°C; a desiccator; an analytical balance capable of weighing to 0.1 mg; and wide-bore pipets.

Dissolved oxygen. An essential compound in natural waters, dissolved oxygen (DO) is necessary to sustain aquatic life and is critical in wastewater treatment process control. The presence or absence of oxygen also determines the "oxidation state" of natural waters, which in turn governs the state in which several pollutants occur in water.

In natural waters, the concentration of DO changes from day to night, and it is useful to measure and report diurnal variations. The frequency of monitoring varies with the purpose. For example, DO concentrations in lakes may be measured once a month whereas those

in influent and effluent streams of a wastewater treatment plant may have to be monitored continuously and recorded electronically.

A common and convenient method of measurement is to use a membrane electrode. The electrode that measures the oxygen concentration is covered with an oxygen-permeable membrane. This feature makes it convenient to use this technique in the field as well as in the laboratory. Commercially available DO meters come with meters that read the DO concentrations in mg/L directly. It is important to calibrate the electrode using the type of sample to be monitored. For fresh, unpolluted waters, the meter can be calibrated with distilled water. For seawaters or estuarine waters, seawater should be used for calibration. The manufacturer's instructions for calibration must be followed.

Biochemical oxygen demand. One of the most common parameters included in any water monitoring system is biochemical oxygen demand (BOD). This parameter is usually defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter in a sample under aerobic conditions (that is, in the presence of oxygen).

Measuring BOD involves a set of standard laboratory procedures that can serve several purposes. For example, the procedures may be used to determine the oxygen requirements for biochemical degradation of organic material (carbonaceous demand) or the oxygen required to oxidize inorganic material such as sulfides and ferrous iron present in wastewater, effluents, and polluted waters. The same methods can be used to measure the oxygen needed to oxidize a reduced form of nitrogen (nitrogenous demand), unless oxidation is prevented by an inhibitor. The BOD test is also used to estimate pollution levels in bodies of surface water and groundwater, and pollution loads from domestic and industrial wastes discharged into natural watercourses. Finally, the test allows analysts to measure the waste loadings of treatment plants and to evaluate the BOD-removal efficiency of these treatment systems.

The sampling frequencies depend on the purpose of the exercise and the type of source where BOD will be monitored. During the initial stages of a monitoring program, the sampling frequencies recommended under normal conditions would be (i) once every two weeks for rivers, (ii) once every two months for lakes, and (iii) once every three months

for groundwater. After sufficient experience has been gained, a statistical analysis of the data can be done to determine if these sampling frequencies should be altered. When measuring the waste load or the removal efficiency of a treatment system, BOD should be monitored at both the inlet and the outlet of the treatment system at least once a day (assuming a continuous flow of input and output of an effluent stream).

To measure BOD, a sample is placed in a full, airtight bottle and incubated at a specified temperature for a specific time. The test involves microbial biochemical reactions that are governed, to some extent, by temperature. This temperature effect is held constant by conducting the test at a specific temperature. Normally the samples are incubated at a temperature of 20°C (which is approximately the median value for natural bodies in temperate countries) for a five-day period. During this time, 70-80 percent of the total organic matter present in the sample is degraded. DO in the sample is measured both initially and after incubation, and BOD is computed from the difference between these two results.

Some samples, such as untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values, may not contain a microbial population sufficient for biodegradation of organic matter. In that case, a population of microorganisms (known as seed) from other sources (for example, an effluent from a biological treatment system) is introduced to ensure biological degradation of organic matter to CO₂ and water.

Since the solubility of oxygen in water is limited (about 9 mg/L at 20°C), waste that is expected to have high amounts of BOD is diluted with distilled or demineralized water (free from any toxic substances such as chlorine, chloramines, or copper). This step ensures that DO is present throughout the period of the test. The dilution water is also aerated to saturate it with oxygen before use.

The apparatus required for the test includes an incubation bottle of 250-300 mL capacity with ground glass stoppers (to prevent trapping of air) and an air incubator or water bath, which is thermostatically controlled at 20±1°C. In the basic test, BOD can be estimated according to the following equation:

$$\text{BOD (mg/L)} = \frac{D1 - D2}{P}$$

When dilution water is seeded,

$$\text{BOD (mg/L)} = \frac{(D1 - D2) - (B1 - B2) \times F}{P}$$

- Where
- D1 = DO of diluted sample immediately after preparation, mg/L
 - D2 = DO of diluted sample after 5 days incubation at 20°C, mg/L
 - P = decimal volumetric fraction of sample used
 - B1 = DO of seed control before incubation, mg/L
 - B2 = DO of seed control after incubation, mg/L
 - F = ratio of seed in diluted sample to seed in seed control
= (% seed in diluted sample)/(% seed in seed control)

Chemical oxygen demand. Chemical oxygen demand (COD) is the amount of oxygen required for complete oxidation of organic matter in a water sample by a strong chemical oxidant. The COD of a water sample is usually related to BOD. Like the BOD test, the COD test is used to estimate the pollution level in surface water and groundwater, and pollution loads from domestic and industrial wastes discharged in natural watercourses. This test is particularly useful once a correlation between COD and BOD has been established, since it is much quicker (usually 2.5 hours) than a BOD test (5 days). After establishing this correlation, the COD test can be substituted for the BOD test. The sampling frequency of COD will then be the same as that for BOD.

Several pieces of apparatus are required when testing for COD. Digestion vessels, which may be borosilicate ampules or borosilicate culture tubes with tetrafluoroethylene (TFE)-lined screw caps, are needed. Other pieces of equipment include a heating block of cast aluminum with holes

to fit the tubes or ampules, and a block heater or oven to operate at $150 \pm 2^\circ\text{C}$. The oven may be used only when it is certain not to affect the tube caps after two hours of exposure at 150°C .

The procedure for testing requires that a known volume of a sample be added to a known volume and concentration of potassium dichromate (a strong chemical oxidant) and concentrated sulfuric acid. The mixture is placed in tubes or ampules and tightly capped with TFE-lined screw caps. The tubes are then heated for two hours at 150°C on a preheated block. Upon cooling, the mixture is titrated against ferrous ammonium sulfate (FAS) of a known concentration. A ferroin indicator (1-2 drops) is used to indicate the end point of the titration, represented by a sharp color change from blue-green to reddish brown. A reagent blank with the same volume of distilled water as in the sample is used to determine the quantity of FAS required to neutralize the quantity of potassium dichromate added to each sample. Typical digestion volumes are as follows: sample (5.0 mL), digestion solution (3.0 mL), sulfuric acid reagent (7.0 mL), and total final volume (15 mL).

The amount of COD in the sample can be determined by the following equation:

$$\text{COD (mg/L)} = \frac{(A - B) \times M \times 8000}{\text{mL sample}}$$

Where A = mL of FAS used for the blank

B = mL of FAS used for sample

$$M = \text{molarity of FAS} = \frac{\text{Volume of potassium dichromate solution titrated}}{\text{Volume of FAS used in titration}} \times 0.10$$

Chlorides. An abundant element on the earth's crust, chlorine occurs as chlorides in the water environment, which lend taste to water. If the corresponding ion with chloride is sodium, water can be distinctly salty at even moderate concentrations. If, however, the corresponding ions are calcium and magnesium, the salty taste does not occur even at

fairly high concentrations. Chlorides can affect metallic pipes, structures, and growing plants.

Chlorides may be monitored along with other anions, such as sulfates, phosphates, nitrates, and nitrites. Quarterly sampling of groundwater should be adequate but more frequent samples (once a month) may be required in streams and rivers. In waters that receive industrial wastes, sampling should occur even more often. Chlorides can be monitored satisfactorily using an ion chromatography technique, which is described in detail in the section on nitrates (nitrogen).

Cyanides. All cyanides are extremely toxic to aquatic life as well as to humans. Hydrogen cyanide (HCN) is especially dangerous.

The sampling frequency for cyanides in natural waters would be once a quarter (roughly the same as for other inorganic parameters). However, more frequent monitoring—typically, once a month or possibly more often—is needed for streams that receive industrial wastes containing cyanides. To determine the efficiency of industrial effluent treatment systems, daily measurement of cyanides is necessary.

When monitoring cyanides, utmost care must be taken not to breathe, touch, or ingest the compound. The procedure for testing must also be carried out under a hood. To determine total cyanides, the sample is first distilled in the presence of acid. Hydrogen cyanide is liberated in the process and absorbed in a sodium hydroxide solution. The cyanide concentration of the resulting solution is then determined colorimetrically.

The cyanide in the sodium hydroxide solution exists as CN^- rather than HCN. The CN^- is treated with chloramine-T at $\text{pH} < 8$ to form CNCl . This gives a red-blue color when a pyridine-barbituric acid reagent is added. The color is proportional to the concentration of the cyanide, which can be compared with standards of known cyanide concentrations to determine the concentration in the sample. The color is read at 578 nm on a spectrophotometer. The colorimetric method is suitable for samples containing 5-20 μg cyanide/L. If the samples contain larger concentrations than 20 μg /L, they can be diluted as necessary.

The apparatus required for distillation includes a 1 L boiling flask with an inlet tube and provision for a water-cooled condenser, a gas absorber with a gas dispersion tube equipped with medium-porosity

fritted outlet, an adjustable heating element with TFE-sleeved ground glass joints or neoprene stoppers and plastic threaded joints for boiling flask, and a condenser. For colorimetric determination, a spectrophotometer that can read at 578 nm with a light path of 10 mm or longer is needed.

Fluorides. These are essential in drinking water for the prevention of dental caries in children. When concentrations in natural waters are low, authorities will often add fluoride to drinking water in water treatment systems. However, when concentrations are high, fluorides can cause fluorosis, a condition that results in the mottling of teeth and damage to bones.

In the case of groundwater that is used for drinking, the concentration of fluorides should be monitored once a quarter. In rivers and streams, it may be monitored more frequently, along with other inorganic parameters of interest.

One method for determining the concentration of fluorides is ion chromatography. However, the results obtained with this technique can be distorted when fluoride exists only at low concentrations and other substances are also present in the water. To avoid this possibility, the colorimetric method is the option outlined here. To eliminate interference effectively, distillation with sulfuric acid may be necessary. The only possible interference after distillation would be chloride, which can be eliminated, if present, by adding silver sulfate to the distilling solution.

When the distilled sample containing fluoride is treated with SPADNS [sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate] reagent and zirconyl acid reagent (zirconyl chloride solution in hydrochloric acid), the mixture produces a color that can be read at 570 nm. The intensity of the color is proportional to the amount of fluoride present in the sample. The sample color is compared with standards of known concentration to determine the concentration of fluoride in the sample. The colorimetric method is applicable for samples containing 0-1.5 mg fluoride/L. If the sample contains higher fluoride concentration, it may be suitably diluted.

Nitrogen. One of the most abundant elements on earth, nitrogen exists in several forms in water. The most reduced state is ammonia (NH_3)

while the most oxidized state is nitrate (NO_3^-). Other forms of nitrogen that exist in natural waters are nitrite (NO_2^-) and organic nitrogen. Organic nitrogen occurs in such natural biochemical compounds as proteins, nucleic acids, and urea and in several synthetic organic compounds. Nitrogen, along with phosphorus, is an essential nutrient for aquatic organisms and often limits the growth of these organisms. However, excessive nitrogen can lead to eutrophication, which results in algal blooms. Excess quantities of nitrates and nitrites in drinking water can cause in infants an illness known as methemoglobinemia or blue-baby syndrome.

Organic nitrogen and NH_3 are usually measured at the same time and, together, are known as "total Kjeldahl nitrogen" or TKN. NH_3 can be measured separately as well, and this procedure is described below. NO_3 and NO_2 can be conveniently measured using an ion chromatograph.

The sampling frequency for monitoring nitrogen under normal conditions could initially be once every two weeks for rivers, once every two months for lakes, and once every three to six months for groundwater. A statistical analysis of the data obtained can then be done to determine whether this frequency should be altered. To determine the nitrogen removal efficiency of a continuously operated wastewater treatment system, all nitrogen forms are monitored at the inlet and outlet of the treatment system once a day.

When monitoring NH_3 , the preferred method applicable for a concentration range of 0.03 mg/L to 1,400 mg/L uses an ammonia-selective electrode. This electrode is commercially available and reads millivolts on the meter. Dissolved ammonium is converted to NH_3 by increasing the pH of the sample to above 11 by adding sodium hydroxide (NaOH). The volume of NaOH added is noted. Standards of known NH_3 concentrations are prepared and millivolt readings are noted to prepare a standard curve. Samples of an unknown concentration are then used and the readings noted. From the standard curve, one can read the concentration when the millivolt values are known. If the sample contains more NH_3 than the range of the test, it is diluted to bring the concentration within the range of measurement for this method.

The concentration of NH_3 can be estimated using the following equation:

$$\text{mg NH}_3 - \text{N/L} = A \times B \times \left[\frac{100 + D}{100 + C} \right]$$

- Where
- A = dilution factor
 - B = concentration of $\text{NH}_3\text{-N/L}$ from the standardization curve
 - C = volume of 10 N NaOH added to the calibration standards, in mL
 - D = volume of 10 N NaOH added to the sample, in mL

NO_3^- and NO_2^- are most conveniently measured using an ion chromatograph. Ion chromatography can be applied to other anions as well. This technique avoids the use of hazardous chemical reagents that are required in the case of other methods. Ion chromatography can be used for most natural waters, as well as for drinking water and wastewater when particles less than 0.2 μm in size have been filtered out. With this method, a small volume of the water sample is injected into an eluent stream and passed through a series of ion exchangers. Anions are separated based on their relative affinities for the ion exchanger. Commercially available ion chromatographs can be used to monitor NO_3^- and NO_2^- and manufacturer's instructions should be followed for the determination.

Organic nitrogen can be measured by the Kjeldahl methods (macro or micro), in which amino nitrogen in organic compounds is converted to ammonium in the presence of sulfuric acid, potassium sulfate, and cupric sulfate (a catalyst). The ammonium is then converted to NH_3 by the addition of an alkali and then distilled. The distilled ammonia is absorbed in boric or sulfuric acid and determined by NH_3 -selective electrode as described earlier. When the sample contains NH_3 as well as organic nitrogen, NH_3 is removed by distillation after addition of a borate buffer and NaOH. The NH_3 concentration in the distillate is determined by the NH_3 -selective electrode. The organic nitrogen concentration is determined by the difference in the ammonia concentrations before and after Kjeldahl digestion.

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Pesticides. Residues of pesticides can be found in storm water runoff from agricultural fields and can contaminate surface water as well as groundwater. A number of these compounds or their degradation products are toxic or carcinogenic and should be monitored. The method described here refers to organochlorine pesticides that have traditionally been used in agriculture.

Surface water and groundwater sources that are used as drinking water sources—especially those that can potentially be contaminated by agricultural runoff—must be monitored once a month, or more often if required. After obtaining and analyzing the initial results, a decision on future monitoring frequency can be made.

The procedure for measuring pesticides in water depends on liquid-liquid extraction and gas chromatography. In liquid-liquid extraction, the pesticides are extracted from the water phase into an organic solvent (or mixture of solvents). After extraction, they are concentrated by evaporating the solvent and reading the sample in a gas chromatograph. In the gas chromatograph, the extracted pesticides are passed along with an inert carrier gas through a column packed with material that adsorbs and desorbs the individual compounds. The time at which the compounds are detected after coming out of the column determines the specific compound, and the amount detected gives the concentration of the compound in the sample. Gas chromatographs are commercially available and can be used for determining pesticides. It is important that the packed column bed and the carrier gas are free of any impurities so that they do not lead to erroneous results. Standards of known pesticide concentrations can be run through the procedure to determine the readings on the recorder. Samples can then be compared with the standards to obtain pesticide concentrations in the samples.

The apparatus required for monitoring pesticides includes glass sampling bottles with TFE-lined screw caps, an evaporative concentrator, separatory funnels, a chromatographic column, and a gas chromatograph equipped with a glass-lined injection port, an electron-capture detector, and a recorder.

The pesticide concentration can be calculated with the following equation:

$$\text{Pesticide concentration } (\mu\text{g/L}) = \frac{A \times B \times C \times D}{E \times F \times G}$$

- Where
- A = nanograms standard pesticide
 - B = peak height of sample (mm or area count on the recorder)
 - C = extract volume (μL)
 - D = dilution factor
 - E = peak height of standard (mm or area count)
 - F = volume of extract injected (μL)
 - G = volume of sample extracted (mL)

Phosphorus. Like nitrogen, phosphorus is an essential nutrient of all life forms and is often a limiting nutrient in natural waters. It usually occurs in natural waters and wastewaters as phosphates—orthophosphates, condensed phosphates, and organically bound phosphates—which may be dissolved or suspended in particles or bodies of aquatic organisms. Since phosphorus is a limiting nutrient, excessive amounts can cause eutrophication of the water body and result in algal blooms. Phosphorus reaches water streams from human and animal waste products, fertilizer runoff from agriculture and farming, and some industrial wastes. As in the case of other inorganic parameters, phosphorus should be monitored more frequently in wastewater treatment plants and less frequently in natural waters.

The procedure for monitoring total phosphorus requires that samples are digested using persulfate in the presence of sulfuric acid. For determination of dissolved phosphorus, the sample is filtered through a $0.45 \mu\text{m}$ filter. Colorimetric analysis using ammonium molybdate, potassium antimonyl tartrate, and ascorbic acid is a common method of phosphorus determination.

Ammonium molybdate and potassium antimonyl tartrate react in the acid medium to form phosphomolybdic acid, which is reduced to molybdenum blue by ascorbic acid. The color formed after this treatment is compared with standards of known phosphorus concentrations. This method is applicable for samples containing 0.01-2.0 mg P/L. For higher

concentrations, the samples can be diluted appropriately. The concentration of phosphates can be satisfactorily determined using an ion chromatograph in the same manner as described in the section on nitrates.

The apparatus required for this test consists of acid-resistant conical flasks that are used for persulfate digestion. Color can be determined with a spectrophotometer that can read at 880 nm.

Sulfates. These occur abundantly in natural waters. They are also present in mine water drainage, which can percolate into groundwater. When associated with sodium and magnesium, sulfates can be cathartic. Sulfates in groundwater may also be reduced to sulfides by bacterial action, and in this form pose additional problems.

Sulfates may be monitored once a quarter in groundwater, but more frequently (once a month) in streams and rivers. In waters that receive industrial wastes, sulfates should be monitored more often.

Sulfates concentration in water samples can be measured by ion chromatography. This technique is described in detail in the section on nitrates.

Sulfides. These compounds commonly occur in groundwater, especially in hot springs. They are also found in domestic and industrial wastewater. Hydrogen sulfide is a foul smelling gas that can be a serious odor nuisance. At high concentrations, it overwhelms the human olfactory system and one stops smelling it. At that concentration, it may be deadly and can kill within a short time. Dissolved hydrogen sulfide is also toxic to aquatic organisms.

Sulfides in groundwater should be monitored once a quarter, but more frequent sampling (once a month) is advisable in streams and rivers. In waters that receive industrial wastes, sulfides may be monitored more often.

Monitoring procedures rely on the fact that sulfides react with dimethyl-*p*-phenylenediamine to produce methylene blue, which can be read at 664 nm on a spectrophotometer. The color obtained from samples of unknown concentration can be compared with that obtained from standard sodium sulfide solutions of known concentrations to determine the sulfide content of the samples. This method is applicable for samples containing 0-1.0 mg sulfide/L. For samples containing higher sulfide concentrations, suitable dilutions must be carried out.

Metals. Though some metals are essential for biological life, others are harmful. Certain metals are beneficial at low concentrations, but toxic at high concentrations. Because metals also affect water and wastewater treatment, they are important in environmental engineering practice.

Because the concentration of metals in the natural environment seldom varies significantly from day to day, an adequate sampling frequency may be monthly, quarterly, or semiannual. For water and wastewater treatment plants, however, weekly or even daily monitoring of influent and effluent samples may be necessary.

The best containers for collecting water samples for metals analysis are made of quartz or TFE. Since such containers are expensive, polypropylene or linear polyethylene bottles with polyethylene caps are frequently used. All bottles should be thoroughly cleaned and washed with metal-free distilled water before use. This step is necessary because metals can occur in nature in minute quantities, and the containers must contain no traces of the metals to be monitored. Though it is preferable to analyze samples as soon as they are collected, they can be preserved easily for up to six months³⁴ by acidification (that is, the addition of concentrated nitric acid to bring the pH of the sample down to less than 2) and storage at 4°C.

Metals can be analyzed using atomic absorption spectrometry. In this technique, the sample is aspirated into a flame and atomized. A light beam is directed through the flame into a monochromator, a device for isolating an absorption line. The atomized element absorbs light, which is detected by a detector. Each metal has its characteristic absorption wavelength. The amount of energy absorbed in the flame at a particular wavelength is proportional to the concentration of the metal in the sample, over a certain concentration range. Different source lamps are used for different metals, which makes the method relatively interference-free. Among the metals that may be of interest, lead, nickel, and arsenic can be easily monitored using this method. For mercury, the preferred method of monitoring is cold-vapor atomic absorption spectrometry. In this case,

³⁴ Mercury is an exception to this generalization.

dedicated laboratory glassware must be available. Glassware that is exposed to mercury during other analyses such as COD, cannot be used since it could contaminate the sample and lead to erroneous results.

The equipment needed for these tests includes an atomic absorption spectrometer (AAS). This instrument contains a light source (a hollow cathode lamp or electrodeless discharge lamp) that emits the line spectrum of an element. A flame for vaporizing the sample is also needed, along with a monochromator or filter, and a photoelectric detector attached to a measuring device and display. For determination of mercury, instruments and accessories specifically designed for mercury are used.

The test procedures require that the AAS be fitted with a lamp specific for the metal to be monitored. Standards of known concentration of the metal are prepared and aspirated into the AAS. The readout in the display is noted for each standard and a standard curve is prepared. The water sample is then aspirated into the device and the readout is noted. This result is compared with the standard curve to obtain the concentration of the metal. For mercury, the manufacturer's instructions on cold-vapor atomic absorption spectrometry are followed.

Oil and grease. Not strictly a single substance, the materials that dissolve in an extracting solvent are referred to as oil and grease (O&G). They interfere with biological wastewater treatment and can reduce treatment efficiency. In natural waters, O&G can form a film above the water surface, thereby reducing the amount of oxygen that can be dissolved into the water from the atmosphere.

The sampling frequency for O&G can initially be the same as for BOD, COD, and DO. If O&G is absent from the samples, the monitoring frequency can be reduced in subsequent tests.

Testing procedures call for the sample to be treated with a solvent (n-hexane or trichlorotrifluoroethane or methyl-tert-butyl ether). Afterwards, the solvent and aqueous phases are separated using a separatory funnel. The O&G is extracted into the solvent phase, the solvent is distilled out of the mixture from a preweighed distillation flask, and the weight of the distillation flask is noted after distillation is complete. The difference in the weight gives the amount of O&G present in the sample.

The apparatus needed for this test includes a separatory funnel with TFE stopcock, a distilling flask, and a distilling adapter.

Radioactivity. Radioactivity is a phenomenon that occurs naturally or is the result of human activities (for example, nuclear power generation, medical and industrial use of radioisotopes, and atmospheric testing of nuclear devices). It causes the ionization of atoms. When this process occurs in the human body, it may affect cells, tissues, and organs. It can also cause cancer.

Locations that are suspected of having been contaminated by radioactive wastes or believed to have natural radioactivity should be sampled more frequently than locations where radioactivity is not found in natural waters. Initially, monitoring may be once every quarter or once every six months.

Radiation is normally measured by a counting instrument that detects and records the expenditure of energy by a radiation event. Gross alpha and beta radiation can be measured using a commercially available thin end-window proportional counter. The samples are prepared for the counters as per the manufacturer's instruction and then placed in the instrument. Radioactivity in a water sample is determined by comparing it with standards having known radioactivity. For alpha radiation, natural uranium/thorium 230 or plutonium 239/americium 241 are used as standards. For beta emissions, strontium 90 in equilibrium with its daughter element yttrium 90 or cesium 137 with its daughter elements barium 137 and metastable barium 137 can be used. Calibration standards must be reported along with gross alpha or beta results.

Gamma radiation is measured using a gamma spectrometer. A standard containing known radionuclide activities is used to determine the counting efficiency of the standard-geometry container in the spectrometer. The sample is then put in this container and gamma spectrum is determined.

The apparatus required for gross alpha and beta emission measurement includes counting pans and a thin end-window proportional counter. The apparatus for detecting gamma radiation consists of a gamma-ray spectrometer, a detector, and a counting container of standard geometry.

Coliforms. The presence of these organisms in water indicates the degree of organic pollution of natural waters (resulting primarily from human and animal waste) and is especially important for issues of sanitation. Coliform organisms comprise several genera of bacteria that produce acid and gas from lactose at 35°C within 48 hours. Fecal coliforms are present in the guts and feces of warm-blooded animals and produce gas from lactose at $44.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$.

The initial sampling frequency for coliforms is the same as that for BOD and COD. If the initial results demonstrate that coliforms are absent from the samples, the frequency for monitoring can be scaled down.

Test procedures require that samples containing coliforms be filtered through sterile membrane filters. After incubation at a specified temperature on an appropriate culture medium (a food source for coliforms to grow), the colonies formed on the filter are counted. Each coliform organism forms a colony around it once the filter is placed on the culture medium. This process requires that all equipment and apparatus be sterilized in an autoclave before use.

When membranes are placed on sterile dishes containing a culture medium, coliforms will form bright red colonies with a metallic sheen within 24 hours of incubation at 35°C on an Endo-type medium. The sheen is due to aldehydes produced as a result of the fermentation of lactose. The formation of aldehydes is an important intermediate step in the formation of acid/gas from lactose. The typical sample size should produce between 20 and 80 colonies on the membrane surface. Coliform colonies can then be counted using a low-power (10-15 \times) microscope with a cool white fluorescent light source. Only colonies with a metallic sheen are counted as coliforms. Other colonies are counted as noncoliforms. For fecal coliforms, the M-FC (membrane-fecal coliform) medium is used and cultures are incubated at $44.5 \pm 0.2^{\circ}\text{C}$. Fecal coliforms form blue colonies, while other bacteria form gray or cream-colored colonies and should not be counted.

The apparatus used in a test for coliforms includes sterile culture dishes, filtration units, sterile membrane filters, an incubator, and an autoclave.

Coliforms are reported as the most probable number (MPN), as expressed in the following equation.

$$\text{MPN}/100 \text{ mL} = \frac{\text{Coliform colonies counted} \times 100}{\text{mL sample filtered}}$$

Estimating Water Discharges

Information on water quality is essential but must be supplemented with additional statistics on the discharge of effluents before public officials can formulate an efficient set of water policies. Regulators need to know which sources are responsible for the discharge of particular pollutants and precisely where these discharges occur.³⁵

The task of identifying individual sources of pollution and linking specific discharges to each source is a complicated one that relies on both surveys and estimation procedures. The difficulties encountered are the main reason why few countries, if any, presently operate discharge-monitoring programs that match their efforts to monitor water quality. Most programs to track the discharge of effluents have a limited geographic coverage, usually focusing only on specific urban areas. Even in these cases, it is rarely possible to put together a comprehensive picture that captures the effects of both human and industrial discharges. Cost is the main barrier to the development of an elaborate monitoring system. To keep expenditures under control, governments rely on a combination of limited, specific surveys and internationally accepted estimation procedures.

Data organization and concepts. To simplify their task, statisticians usually identify discharges by source and type of emitter. Discharges may come from either from point sources or diffuse sources.

³⁵ Information on where emissions occur can be used to determine the location and type of wastewater treatment facilities that are needed.

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Pollution from point sources is mainly associated with the release of wastewater from municipal, agro-industrial, and industrial sites. In countries where mining operations are significant, these activities can also release substantial amounts of wastewater. Pollution from diffuse sources either is spread over large areas or cannot be directly attributable to specific activities. Examples of diffuse sources are pesticides and their decay products contained in surface runoffs, and nitrogen and phosphorus released from fertilizers and animal wastes. These pollutants eventually reach water bodies through runoffs from storms and atmospheric deposition. Effluent discharges by point sources are relatively concentrated and readily identified. It is comparatively easy to estimate the amount of pollutants from point sources and to control their discharges. Pollution from diffuse sources is much more difficult to assess and manage.

In addition to the two pollution sources, statisticians generally focus on three types of emitters:

- (i) Productive activities typically account for the bulk of all discharges, the majority of which are from point sources. Some of the pollutants released by industrial activities consist of biodegradable matter, but other nonbiodegradable substances are also found, depending on the product and production process. Agricultural discharges are generally in the form of manure, fertilizers, and pesticides. These compounds, which are spread over large areas of arable land, reach the water through runoff and represent a diffuse source of pollution.
- (ii) Households are a second source of effluent discharges. The household sector is responsible for the release of urine and feces, as well as water from washing, personal care, and kitchen activities. The discharges consist mainly of biodegradable matter.
- (iii) Runoffs from roofs, roads, and other impermeable surfaces are a third type of discharge. Heavy metals and various forms of accumulated debris are often washed away by rain as part

of surface runoff. In some instances, urban storm runoff can be a significant contributor to pollution, even accounting for a larger share of the total pollution load than the untreated sewage of the same community.

Treatment of wastewater.³⁶ Any program to monitor the discharge of effluents should take into account the role of existing systems for treatment of wastes and water purification. Treatment plants must be established to treat raw wastewater before it is released into ambient waters. If the system for treatment of sewerage is rudimentary (for example, consisting of little more than the use of settlement ponds), biodegradable matter may not be removed and secondary biological treatment is required. Industrial establishments may also be required to modify their production processes by introducing new, low-waste technologies and methods of recycling wastewater.

The major categories of water discharges and treatment methods are the following:

- (i) direct discharges released without treatment as well as discharges that may or may not have been subjected to treatment;
- (ii) discharges from pits (collected periodically) and dumped, either without treatment or treated after collection;³⁷ and
- (iii) discharges generated by wastewater treatment plants.

To establish a relationship between the data on discharges and the data gathered from monitoring water quality, the discharge points for treated and untreated wastes must be specified.

³⁶ The following discussion draws on ESCAP (1999), Chapter 5.

³⁷ In the absence of a sewerage system, household wastes may be periodically collected from latrines and emptied into pits. These pits often leak or spill over excess fluid into the surrounding soil and therefore pose a threat to groundwater.

BOD is the preferred parameter for gauging the need for general wastewater treatment (see the section Monitoring the Quality of Surface Water). For household wastewater, this parameter, alone, is considered as sufficient. However, in the case of industrial discharges and runoffs from hard surfaces, other pollutants should be involved, including heavy metals and pesticides. If hazardous wastes are also present, it may be necessary not only to monitor discharges but also to track the final destinations of these pollutants. Eventually, the monitoring program may have to be expanded to cover raw waste and sludge as well as the major sources of water pollution.

Statistical methods. As already noted, most programs to monitor discharges are confined to urban areas and the discussion here follows that practice. Three components—industries, households, and wastewater treatment facilities—figure prominently in the calculation of water discharges. Industrial establishments are usually clustered around major cities and account for a significant proportion of all discharges. The sheer number of households helps to explain the volume of pollutants attributed to this sector. The composition, size distribution, and types of pollutants associated with these two groups naturally differ and the statistical methods employed must take these characteristics into account.

The role played by wastewater treatment plants is obviously different from that of the two major sets of emitters. The purpose of these plants is to reduce the amount of waste in the influents entering the water system. Much depends on the type of technology employed. The more effective a particular method of treatment is, the greater the reduction of the influent load. Thus, statisticians must have some idea of how well treatment plants perform so as to estimate the effluent load.

The coefficients used to estimate effluent discharges and reductions in the influent load are the heart of any monitoring system. The statistical methods used to develop these coefficients differ for each of the three components noted here. In the case of the industry sector, there is ample evidence to indicate that the largest establishments are responsible for up to 80 percent of all industrial discharges in developed countries, and the figure should be comparable for developing countries. Each industrial establishment represents a point source of discharges, but the coefficients

for major polluters are the most important and should receive the most attention.

The population of industrial establishments in an urban area is usually too large to consider any direct method of measuring effluent discharges for every polluter. The exercise can be simplified by dividing the urban industry sector into subgroups that can be more easily handled by a few estimation routines. Several criteria could be used for this purpose.³⁸ However, because economic statistics are expressed in monetary units and the number of employees, these measures offer the most practical (and cheapest) means of defining different subgroups.

With the help of economic statistics, the industrial establishments in an urban area can be divided into two or three categories. Decisions regarding the boundaries between categories should be made after studying the current size distribution of all industrial establishments. An illustrative breakdown is given below, but, in practice, the dividing lines between categories will depend on the characteristics of the industry sector.

Small producers may be identified as those with less than 25 employees, less than 10, or less than 5. Generally, economic information on this group is scanty. Some industrial surveys include a sample of small producers and if this information is available, the same cutoff point can be adopted here. Effluent discharges can be estimated for this group on the basis of the workforce if labor surveys or censuses provide this data.

Producers of intermediate size may be defined as establishments with 25-100 employees. Generally, more information will be available for this group than for smaller producers, and physical, monetary or employee data can be used to estimate discharges. If the statistical program of the NSO includes occasional sample surveys of these firms, additional questions should seek data on the release of wastewater, input and output coefficients, relevant features of the production process, and wastewater treatment.

³⁸ Input-output coefficients would be a more logical source of information for the development of these criteria but few countries have an up-to-date input-output table, especially one expressed at a sufficient level of detail.

Large producers will include all the remaining firms (in this case, those with more than 100 employees). Ideally, this subset should be the subject of a special survey, and effluent-discharge coefficients for each firm should be determined in a direct manner. If sufficient resources are not available to mount a special survey, other options can be considered. Should the total number of large firms be too great or too widely dispersed to survey all, a subset can be identified. To be representative, the subset should take into account both the location and the industries involved. The list of firms to be surveyed can also be restricted to a smaller geographic area and to just a few types of industries. Another alternative is to add relevant questions to any recurrent survey program for firms in this size category.³⁹

The large number of households in an urban area make it impractical to consider any direct method of estimating discharges. Generally, the distribution and composition of urban households differ markedly from national averages and the pattern in the rural sector. Household surveys and population censuses can be consulted to obtain some idea of these characteristics. A problem unique to the household sector is the role of slums and squatter settlements. Few household statistics consider this subset and, if they are included, the data may be lumped together with other figures under the heading of "marginal housing." In either case, it will be very difficult to determine the relevant characteristics of this group and a special survey may be needed.

Researchers have noted several characteristics that should be borne in mind.⁴⁰ First, the release of effluents into water by rich and poor households will be similar in several ways, but differences in the wastewater streams of the two groups will be significant. Rich households tend to use more water for washing and bathing, in part owing to the availability of piped water. Second, methods for wastewater disposal, treatment, and release can be markedly different for rich and poor households. In slum

³⁹ Questions to be appended to an existing survey might refer to physical input/output coefficients, water usage and sources, wastewater treatment, financial outlays in environmental protection, and so on.

⁴⁰ See, for example, ESCAP (1999), Chapter 5.

areas, wastewater is often released directly into the environment through open sewers or pit latrines. Third, household surveys are a possible source of information on methods of sewage collection and treatment. Firms engaged in communal waste disposal and treatment services may also be able to supply data or advice that will be helpful in constructing estimates.

The ultimate goal of the exercise is usually to estimate discharges of BOD per household. Statisticians usually begin by classifying the urban household population according to the water treatment system being used. Discharge coefficients—expressed in grams of BOD per person per day—can then be determined for each group. Discharges of BOD per household can be expressed in terms of the following equation:

$$\begin{aligned} \text{Discharge of BOD per household} = \\ \text{Standard emission factor} * \text{number of persons} * \text{socio-economic} \\ \text{correction factor} * \text{treatment degree correction factor.} \end{aligned}$$

The socioeconomic correction factor refers to the total amount of wastewater produced (expressed in grams of BOD). The treatment correction factor applies to the type of wastewater treatment used. This subject is discussed below and examples of correction factors are given.

To compute the effluent load, statisticians must first determine the extent to which influents have been reduced by wastewater treatment. The simplest and most rudimentary form of treatment, which is known as the primary method, merely separates settleable materials from the wastewater. If a secondary or biological treatment process is also used, organic material is mineralized through the action of bacteria and the level of BOD is further reduced. When a third or tertiary process is available, selected minerals such as phosphorus are removed by binding them to insoluble substances. In many developing countries, wastewater treatment—if it exists at all—is limited to primary treatment, owing mainly to cost considerations.⁴¹

⁴¹ Primary treatment will not significantly reduce coli bacteria and other serious contaminants. Significant reduction can be achieved only with secondary treatment.

Illustrative values for effluent discharges and pollution reduction factors are shown in Table 5.2. Secondary treatment is clearly more effective than primary treatment. In fact, primary treatment does very little to reduce the amounts of potassium and nitrogen compounds in wastewater. Many of the values in the table have a rather large range, suggesting that estimations specific to each urban area are preferable to the use of benchmark values.

Table 5.2: Examples of Emission Factors and Pollution Reduction Factors for Household Waste

Parameter	Emission Factor	Pollution Reduction Factors (percentage reduction)	
		Primary Treatment	Secondary Treatment
Volume (in liters per capita per day)	20-300 ^a		
BOD	45-54 ^b	5-35	50-98
P	0.6-4.5 ^b	0-10	10-85 ^c
N	6-12 ^b	0-7.5	15-50

^a The lower value applies to households with septic tanks.

^b Figures are in grams per capita per day.

^c The highest rate applies to tertiary treatment with chemical precipitation or coagulation.

Source: Economopoulos (1993), Table 4.2.2.

Water Quantity and Uses

Water stress, which refers to pressure on both the quantity and quality of water resources, has a profound influence on human activities. Adequate water management is essential to ensure that water supplies

are available and sufficiently reliable to support all kinds of economic activities and water-dependent ecosystems. Most countries regularly and systematically collect and analyze hydrological and hydrogeological data. Because several agencies are typically responsible for these operations, the information on quality and quantity is not integrated. As a result, policy making and planning for water quantity and quality management are often fragmented.

A country's renewable supply of water is derived from two sources:

- (i) rainfall that falls directly on its land area, and
- (ii) river water originating from outside the country (external water sources).

The total annual internal renewable water resources of a country is defined as the sum of the annual average freshwater flow of rivers and the groundwater produced from rainfall within the country's borders. Roughly two thirds of this total becomes flood runoff. Only the remaining third is available as usable surface and underground water supplies. Nor is the volume of available water distributed evenly, either throughout the year or between parts of the country. There are both seasonal and spatial variations in supply and the former may be especially significant in the case of river flows.⁴²

Water supply. Problems of water scarcity arise when the demand exceeds the supply for any significant period. Shortages occur most frequently in areas with low rainfall or high population density, and in areas with intensive agricultural or industrial activity. In addition to water shortages, overexploitation of water can result in the drying out of natural areas, and to saltwater intrusion in aquifers.

⁴² It is important that statisticians assess of this seasonal variation, which is usually expressed as average monthly river flows. Recorded river flows can also be combined with data on the catchment area to develop indicators of water flow (or runoff) per unit area.

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The source of all internal groundwater is rainfall, part of which recharges the groundwater. Groundwater supplies rivers with a base flow during months without rainfall. The inability to adequately recharge groundwater (because of soil compaction or removal of vegetation) is an important factor contributing to droughts and agricultural failures and should be monitored closely.

Normally, each country operates a network of rainfall and river-flow measuring stations. To simplify the task, attention usually focuses on the larger and more stationary water bodies for which long-term availability can be most easily determined. Problems arise nonetheless because groundwater represents a natural reservoir with a stored volume, inflows, and outflows. Estimates of groundwater volume (expressed in terms of exploitable potential per year) can usually be constructed through analysis.⁴³ Data on outflows is derived from records of groundwater withdrawal (pumping) and measurements of river base flows. However, data for inflows is much more difficult to obtain and is available in only a few countries.

The agencies responsible for collecting information (for example, the department of public works or the department of irrigation) routinely analyze the raw data to derive totals, averages, measures of dependable flow, and time series indicators (including indicators of rainfall intensity). Some of the measures developed may be rather detailed. For instance, available water can be defined as the volume flowing in a river that is available at least 90 percent of the time.

Water usage. Estimates of water availability, however crude, give some idea of supply and can be used in conjunction with data on water utilization. Information on water use is subdivided into two categories:

- (i) Consumptive use. This involves the removal of water from its source. Statistics on consumptive use are usually reported as water withdrawals by sector (agriculture, industry,

⁴³ Local changes in usable groundwater volume can be determined from measurements of the depth of the water table or changes in pressure levels for pressurized aquifers.

household, and so on). Consumptive use data can also be identified by source: surface water or groundwater. Groundwater is an important source for domestic use since the quality is usually superior to that of surface water.

- (ii) Nonconsumptive use. Examples falling into this category include hydropower generation, fisheries, navigation, and recreation. Nonconsumptive use does not entail water removal and data are not reported in terms of use rates or volumes, but rather in the form of values derived from the use (for example, electricity generation by hydropower plants).

At the national level, two aggregate measures of water quantity are popular. One, a measure of the renewable water resources, is an aggregate annual figure that is used mainly as a basis for developing indicators of water supply availability. A critical level of use is reached when the rate of water withdrawal reaches or exceeds the average annual available water supply. A second measure is the ratio of available water supply to the total population. With this indicator, countries can be ranked according to relative available water per capita or scarcity.

The pattern of water use depends on a number of determinants, but at the macroeconomic level the most important are probably the level of development, the composition of economic activities or the structure of the economy (a factor which, in turn, is related to level of development), and climate. In the EU, agriculture and cooling needs account for nearly two thirds of all water use. European countries with warm climates may abstract more than a quarter of their freshwater resources each year. About 80 percent is consumed and is therefore not available for other purposes. Most of this water is thought to be used for irrigation in agriculture, but no data is available. Instead, statisticians use the land area subject to irrigation as a proxy. The situation is different when abstracted water is used for cooling. In that case, the water is returned and can be used again.

Water use by households and industry has been falling in many developed countries for more than a decade.⁴⁴ There are a number of reasons for this decline, including greater awareness of water use, water metering, increased water charges and taxes, restrictions on garden watering, fewer leaks, and widespread use of more efficient appliances such as low- or dual-flush toilets. Groundwater is the source for as much as three quarters of the public water supply in developed countries. It is increasingly preferred as public water supply because it is generally of higher quality than surface water and requires less treatment. This preference has led to overabstraction and a lowering of the groundwater table in many developed countries. The consequences are the drying up of spring-fed rivers, destruction of many wetlands, and saltwater inflow to aquifers.

No comparable information on such trends is available in most developing countries. Many compile little or no information on water uses. The situation could be different, depending on domestic policies, economic structure and other determinants. However, proper management of reservoirs, groundwater reserves and surface water is essential. Without controls, problems of water stress are bound to mount in the longer term.

⁴⁴ In the EU, for example, the amount of water abstracted from public water supplies declined by around 10 percent during the 1990s.