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Chapter 3* - Selection of water quality variables

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3.1. Introduction

The selection of variables for any water quality assessment programme depends upon the objectives of the programme (see Chapters 1 and 2). Appropriate selection of variables will help the objectives to be met, efficiently and in the most cost effective way. The purpose of this chapter is to provide information which helps the appropriate selection of variables. Each variable is discussed with respect to its origins, sources, behaviour and transformations in the aquatic system, the observed ranges in natural and polluted freshwaters, the role of the variable in assessment programmes, and any special handling or treatment of samples that is required. The final section of this chapter suggests some combinations of variables which might be used for different water quality assessment purposes. These can be used as a basis for developing individual programmes.

The methods employed to measure the selected variables depend on access to equipment and reagents, availability of technical staff and their degree of expertise, and the level of accuracy required by the objectives of the programme (see Chapter 2). A summary of the principal analytical methods for major variables is given in Table 3.1 and a summary of pre-treatment and storage of samples for different analyses is given in Table 3.2. Detailed descriptions of sampling and analytical methods are available in the companion volume to this guidebook by Bartram and Ballance (1996) and in a number of standard reference guides published by various international organisations and programmes, or national agencies (e.g. Semenov, 1977; WHO, 1992; NIH, 1987-88; Keith, 1988; APHA, 1989; AOAC, 1990). In addition a world-wide federation of national standards bodies and international organisations, the International Standards Organization (ISO), publishes a series of approved “International Standards” which includes methods for determining water quality. Further detailed information on the study and interpretation of chemical characteristics in freshwaters is available in Hem (1989), Environment Canada (1979) and many other specialist texts.

3.2. Hydrological variables

Determining the hydrological regime of a water body is an important aspect of a water quality assessment. Discharge measurements, for example, are necessary for mass flow or mass balance calculations and as inputs for water quality models.

Table 3.1. Analytical methods for determination of major chemical variables

Variable	Simple						Advanced					Sophisticated				
	Gravimetric	Titrimetric	Visual	Photometric	Electrochem. probe	Flame photometry	UV-VIS and IR	Fluorimetry	AES	AAS GC	Flow injection	Stripping VA	ICP-AES	IC	LC	GC/MS
Residue	L															
Suspended matter			F	FL												
Conductivity					FL											
pH			F		FL											
Acidity, alkalinity		L														
Eh					F											
Dissolved oxygen		L			F											
CO_2		L			F											
Hardness		L														
Chlorophyll *a*				L			L	FL								
Nutrients			F	L	FL						L			L		
Organic matter (TOC, COD, BOD)		L			FL		L									
Major cations			F		FL	L				L				L		
Major		L	F	L	FL									L		

anions																
Sulphide		L		L										L		
Silica				L												
Fluoride				L	FL									L		
Boron				L												
Cyanide				L							L			L		
Trace elements			F	L					L	L	L	L	L			
Mineral oil	L						L	L								
Phenols				L						L					L	L
Pesticides										L					L	L
Surfactants			F	L								L				
Other organic miicropollutants								L		L					L	L

F	Field methods
L	Laboratory methods
TOC	Total organic carbon
COD	Chemical oxygen demand
BOD	Biochemical oxygen demand
UV-VIS	Ultraviolet and visual spectrophotometry
IR	Infra-red spectrography
AES	Atomic emission spectrophotometry
AAS	Atomic absorption spectrophotometry
GC	Gas chromatography
VA	Voltammetry
ICP-AES	Inductively coupled plasma atomic emission spectrometry
IC	Ion chromatography
LC	Liquid chromatography
GC/MS	Gas chromatography/mass spectrometry

Table 3.2. Pretreatment and storage requirements of samples for laboratory determination of chemical variables (see text for further details)

Variable	Pretreatment						Type of bottles		Conditions of storage				Max. time of storage prior to analysis			
	None	Filtration	Chemical stabilisation	Acidification	Alkalinisation	Solvent extraction	Glass	Polyethylene	Dark	Cold (approx. 4°C)	Frozen (max. -15° C)	Minimum possible	24 hours	3 days	1 week	3 weeks
Residue	x						x					x				
Suspended matter	x						x	x	x				x			
Conductivity		x					x	x					x			
PH	x						x	x				x				
Acidity, alkalinity	x						x	x				x				
DO (Winkler method)			x						x			x				
CO_2	x						x					x				
Hardness (general)		x					x	x								
Chlorophyll *a*			x					x	x	x		x				
Chlorophyll *a* and POC		x									x					x[1]
Nutrients[2]			x				x		x	x			x			
TOC				x			x		x	x					x	
COD				x			x			x			x			
BOD	x						x		x	x		x				
Na^+, K^+		x						x								
Ca^{2+}, Mg^{2+}		x		x				x								

Major anions	x						x	x								
Sulphide			x				x		x					x		
Silica	x							x	x	x					x	
Fluoride	x							x							x	
Boron	x							x								
Cyanide					x			x		x		x				
Trace elements (dissolved)		x		x				x								
Mineral oil						x	x		x	x						
Phenols					x		x			x				x		
Pesticides						x	x				x					x
Other organic micropollutants						x	x			x				x		

Where no indication is given under column headings, no special conditions of pretreatment or storage are necessary.

Sample bottles for many variables require special cleaning, particularly those for trace metals and organic micropollutants. Requirements for special cleaning are described in operational manuals for analytical methods (e.g. WHO, 1992).

DO Dissolved oxygen
POC Particulate organic carbon
TOC Total organic carbon
COD Chemical oxygen demand
BOD Biochemical oxygen demand

[1] When frozen

[2] NO_3^-, NH_4^+, PO_4^{3-}, total P

3.2.1. Velocity

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

movement of compounds (particularly pollutants) within water bodies, including groundwaters. For example, knowledge of water velocity enables the prediction of the time of arrival downstream, of a contaminant accidentally discharged upstream.

Water velocity can vary within a day, as well as from day to day and season to season, depending on hydrometeorological influences and the nature of the catchment area. It is important, therefore, to record the time when measurements are taken and every attempt should be made to measure velocity at the same sites as other water quality samples are collected. Velocity is determined (in $m\ s^{-1}$) with current meters or tracers, such as dyes. Measurements are usually averaged over a period of 1-2 minutes.

3.2.2. Discharge

The discharge is the volume flowing for a given period of time. For rivers, it is usually expressed as $m^3\ s^{-1}$ or $m^3\ a^{-1}$. The amount of suspended and dissolved matter in a water body depends on the discharge and is a product of the concentration and the discharge. Natural substances arising from erosion (suspended matter) increase in concentration exponentially with increased discharge (see Figure 6.11A and section 6.3.3). Substances introduced artificially into a water body, such as trace elements and organic matter, tend to occur at decreasing concentrations with increasing river discharge. If a pollutant is introduced into a river at a constant rate, the concentration in the receiving water can be estimated from the quantity input divided by the river discharge (see the example in Figure 6.13). Sedimentation and resuspension (see Chapter 4) can, however, affect this simple relationship.

Discharge can be estimated from the product of the velocity and the cross-sectional area of the river. It should be measured at the time of sampling and preferably at the same position as water samples are taken. As cross-sectional area varies with different discharges, a series of measurements are needed in relation to the different discharges. Measurements of depth across a transect of the water body can be used to obtain an approximate cross-sectional area. Specific methods for calculating discharge are available in WMO (1974, 1980).

3.2.3. Water level

Measurement of water level is important to determine the hydrological regime of lakes, reservoirs and groundwaters and the interaction between groundwaters and surface waters. Measurement of water level is necessary for mass flow calculations in lakes and groundwaters and must be measured at the time and place of water sampling.

Water can flow to or from an aquifer which is in continuity with a river, depending on the relative water levels in the river and aquifer. Low water levels in the river can induce groundwater flow to the river, and high water levels can reverse the flow and produce losses from the river to the aquifer. Similarly, when groundwater levels are low (or deep) surface water infiltrates downwards to the water table (see Chapter 9). Depending on the relative water levels in the aquifer and river, stretches which gain or lose may occur in the same river. Also a particular stretch may be gaining at one time of year and losing at another, as river levels change with the seasons. As the river water and groundwater may be of very different qualities, significant variations in water quality may be

experienced in wells close to rivers, and in the river itself. Measurement of groundwater levels is particularly important in relation to saline intrusion.

3.2.4. Suspended matter dynamics

Suspended particulate matter consists of material originating from the surface of the catchment area, eroded from river banks or lake shores and resuspended from the bed of the water body. Measurement of suspended matter transport is particularly important where it is responsible for pollutant transport and in such cases its measurements should be undertaken frequently (see Chapter 4). Usually sediment concentration and load increase exponentially with discharge (see Figure 6.11A). Particles may also settle, or be resuspended, under different discharge conditions.

Suspended matter concentrations should be measured along with the other hydrological variables. In rivers of uniform cross-section, a single sample point may be adequate, whereas for other rivers, multiple point or multiple depth, integrated sampling is necessary. Such samples should be taken at the same points as water velocity measurements and other water quality samples. In addition to analysing suspended matter as described in sections 3.3.4 and 3.3.5, grain size should be determined. Whenever possible, samples from bottom sediments should also be examined.

3.3. General variables

3.3.1. Temperature

Water bodies undergo temperature variations along with normal climatic fluctuations. These variations occur seasonally and, in some water bodies, over periods of 24 hours. Lakes and reservoirs may also exhibit vertical stratification of temperature within the water column (see Chapters 7 and 8).

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

Surface waters are usually within the temperature range 0° C to 30° C, although “hot springs” may reach 40° C or more. These temperatures fluctuate seasonally with minima occurring during winter or wet periods, and maxima in the summer or dry seasons, particularly in shallow waters. Abnormally high temperatures in surface water can arise from thermal discharges, usually from power plants, metal foundries and sewage treatment plants. Ground-water usually maintains a fairly constant temperature which,

for surficial aquifers, is normally close to the mean annual air temperature. However, deep aquifers have higher temperatures due to the earth's thermal gradient.

Temperature should be measured *in situ,* using a thermometer or thermistor. Some meters designed to measure oxygen or conductivity can also measure temperature. As temperature has an influence on so many other aquatic variables and processes, it is important always to include it in a sampling regime, and to take and record it at the time of collecting water samples. For a detailed understanding of biological and chemical processes in water bodies it is often necessary to take a series of temperature measurements throughout the depth of the water, particularly during periods of temperature stratification in lakes and reservoirs (see Chapters 7 and 8). This can be done with a recording thermistor linked to a pressure transducer, directly reading temperature with depth, or by reversing thermometers built into a string of sampling bottles, or by direct, rapid measurements of water samples taken at discrete depths.

3.3.2. Colour

The colour and the turbidity (see section 3.3.5) of water determine the depth to which light is transmitted. This, in turn, controls the amount of primary productivity that is possible by controlling the rate of photosynthesis of the algae present. The visible colour of water is the result of the different wavelengths not absorbed by the water itself or the result of dissolved and particulate substances present. It is possible to measure both true and apparent colour in water. Natural minerals such as ferric hydroxide and organic substances such as humic acids give true colour to water. True colour can only be measured in a sample after filtration or centrifugation. Apparent colour is caused by coloured particulates and the refraction and reflection of light on suspended particulates. Polluted water may, therefore, have quite a strong apparent colour.

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

Colour can be measured by the comparison of water samples with a series of dilutions of potassium chloroplatinate and crystalline cobaltous chloride. The units are called platinum-cobalt units based on 1 mg l^{-1} Pt. Natural waters can range from < 5 in very clear waters to 300 units in dark peaty waters. The total absorbance colour (TAC) method measures integrated absorbance of the filtered sample (pH 7.6) between 400 and 700 nm and the true colour (TUC) is determined by measuring the absorbance at 465 nm. One TAC unit is equivalent to the colour of 2 mg l^{-1} Pt. The TAC units range from 1 to 250. As the compounds determining the colour of the water are not very stable, measurements should be made within two hours of collection.

3.3.3. Odour

Water odour is usually the result of labile, volatile organic compounds and may be produced by phytoplankton and aquatic plants or decaying organic matter. Industrial and human wastes can also create odours, either directly or as a result of stimulating biological activity. Organic compounds, inorganic chemicals, oil and gas can all impart

odour to water although an odour does not automatically indicate the presence of harmful substances.

Usually, the presence of an odour suggests higher than normal biological activity and is a simple test for the suitability of drinking water, since the human sense of smell is far more sensitive to low concentrations of substances than human taste. Warm temperatures increase the rate and production of odour-causing metabolic and decay products. Different levels of pH may also affect the rate of chemical reactions leading to the production of odour.

Odour can be measured in terms of the greatest dilution of a sample, or the number of times a sample has to be halved with odour-free water, that yields the least definitely perceptible odour. The former method is known as the Threshold Odour Number (TON) and the latter method as the Odour Intensity Index (OII). Both methods suffer from the subjective variability of different human judges.

3.3.4. Residue and total suspended solids

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

Residue determination is based on gravimetric measurement after following the appropriate procedures, i.e. filtration, evaporation, drying and ignition. The results of residue determination depend on the precise details of these procedures. Total suspended solids are the solids retained on a standard filter (usually a glass fibre “GF/C” grade) and dried to a constant weight at 105° C (Bartram and Ballance, 1996).

To achieve reproducibility and comparability, care must be taken in following the appropriate methods. For further details see WHO (1992) and Bartram and Ballance (1996). Samples should preferably be kept in hard-glass bottles until analysis can be performed, although polythene bottles can be used if the suspended material does not stick to the walls of the bottle. To help prevent precipitation occurring in the sample bottles they should be completely filled and then analysed as soon as possible after collection.

3.3.5. Suspended matter, turbidity and transparency

The type and concentration of suspended matter controls the turbidity and transparency of the water. Suspended matter consists of silt, clay, fine particles of organic and inorganic matter, soluble organic compounds, plankton and other microscopic organisms. Such particles vary in size from approximately 10 nm in diameter to 0.1 mm in diameter,

although it is usually accepted that suspended matter is the fraction that will not pass through a 0.45 µm pore diameter filter (see Chapter 4). Turbidity results from the scattering and absorption of incident light by the particles, and the transparency is the limit of visibility in the water. Both can vary seasonally according to biological activity in the water column and surface run-off carrying soil particles. Heavy rainfall can also result in hourly variations in turbidity. At a given river station turbidity can often be related to TSS, especially where there are large fluctuations in suspended matter. Therefore, following an appropriate calibration, turbidity is sometimes used as a continuous, indirect measurement for TSS.

Transparency can be measured easily in the field and is, therefore, included in many regular sampling programmes, particularly in lakes and reservoirs, to indicate the level of biological activity. It is determined by lowering a circular disc, called a Secchi disc, on a calibrated cable into the water until it just disappears. The depth at which it disappears, and just reappears, is recorded as the depth of transparency. A Secchi disc is usually 20-30 cm in diameter (although the result is not affected by the disc diameter), and coloured white or with black and white sectors.

Turbidity should be measured in the field but, if necessary, samples can be stored in the dark for not more than 24 hours. Settling during storage, and changes in pH leading to precipitation, can affect the results during storage. The most reliable method of determination uses nephelometry (light scattering by suspended particles) by means of a turbidity meter which gives values in Nephelometric Turbidity Units (NTU). Normal values range from 1 to 1,000 NTU and levels can be increased by the presence of organic matter pollution, other effluents, or run-off with a high suspended matter content. A visual method of determination is also available in Jackson Turbidity Units (JTU), which compares the length of the light path through the sample against a standard suspension mixture.

3.3.6. Conductivity

Conductivity, or specific conductance, is a measure of the ability of water to conduct an electric current. It is sensitive to variations in dissolved solids (see section 3.3.4), mostly mineral salts. The degree to which these dissociate into ions, the amount of electrical charge on each ion, ion mobility and the temperature of the solution all have an influence on conductivity. Conductivity is expressed as microsiemens per centimetre (µS cm^{-1}) and, for a given water body, is related to the concentrations of total dissolved solids and major ions (see Figure 10.14). Total dissolved solids (in mg l^{-1}) may be obtained by multiplying the conductance by a factor which is commonly between 0.55 and 0.75. This factor must be determined for each water body, but remains approximately constant provided the ionic proportions of the water body remain stable. The multiplication factor is close to 0.67 for waters in which sodium and chloride dominate, and higher for waters containing high concentrations of sulphate.

The conductivity of most freshwaters ranges from 10 to 1,000 µS cm^{-1} but may exceed 1,000 µS cm^{-1}, especially in polluted waters, or those receiving large quantities of land run-off. In addition to being a rough indicator of mineral content when other methods cannot easily be used, conductivity can be measured to establish a pollution zone, e.g. around an effluent discharge, or the extent of influence of run-off waters. It is usually measured *in situ* with a conductivity meter, and may be continuously measured and

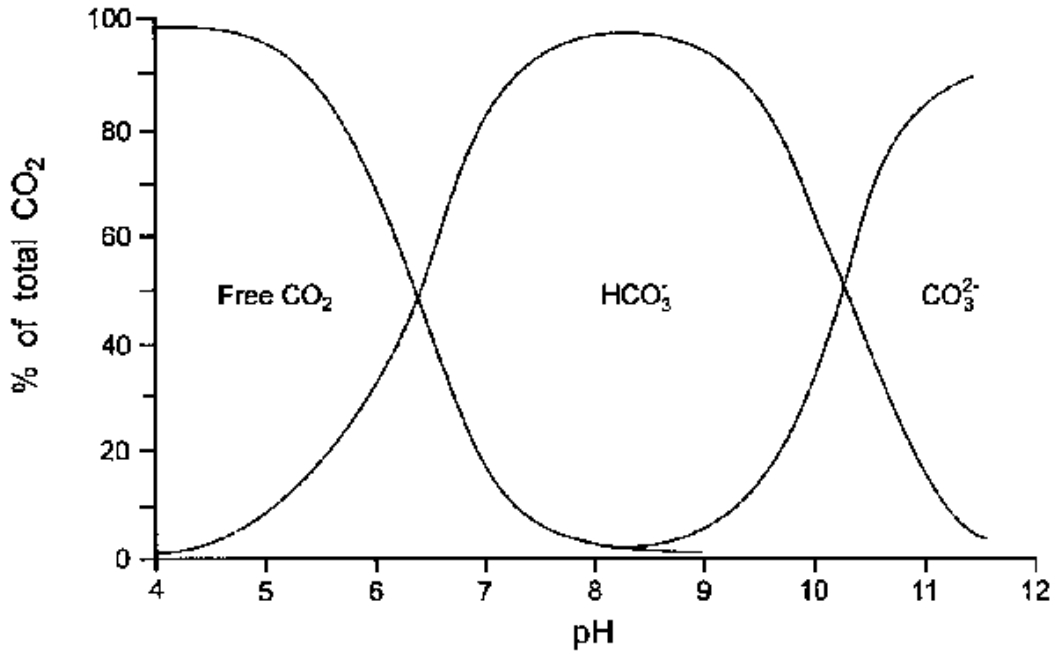
recorded. Such continuous measurements are particularly useful in rivers for the management of temporal variations in TDS and major ions.

3.3.7. pH, acidity and alkalinity

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

The pH is a measure of the acid balance of a solution and is defined as the negative of the logarithm to the base 10 of the hydrogen ion concentration. The pH scale runs from 0 to 14 (i.e. very acidic to very alkaline), with pH 7 representing a neutral condition. At a given temperature, pH (or the hydrogen ion activity) indicates the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compounds and biochemical processes in the solution. In unpolluted waters, pH is principally controlled by the balance between the carbon dioxide, carbonate and bicarbonate ions (see Figure 3.1) as well as other natural compounds such as humic and fulvic acids. The natural acid-base balance of a water body can be affected by industrial effluents and atmospheric deposition of acid-forming substances. Changes in pH can indicate the presence of certain effluents, particularly when continuously measured and recorded, together with the conductivity of a water body. Diel variations in pH can be caused by the photosynthesis and respiration cycles of algae in eutrophic waters (see Figure 6.19). The pH of most natural waters is between 6.0 and 8.5, although lower values can occur in dilute waters high in organic content, and higher values in eutrophic waters, groundwater brines and salt lakes.

Figure 3.1. The relative proportions of different forms of inorganic carbon in relation to the pH of water under normal conditions



Acidity and alkalinity are the base- and acid-neutralising capacities (ANC) of water and are usually expressed as mmol l^{-1}. When the water has no buffering capacity they are inter-related with pH. However, as most natural waters contain weak acids and bases, acidity and alkalinity are usually determined as well as pH. The acidity of water is controlled by strong mineral acids, weak acids such as carbonic, humic and fulvic, and hydrolising salts of metals (e.g. iron, aluminium), as well as by strong acids. It is determined by titration with a strong base, up to pH 4 (free acidity) or to pH 8.3 (total acidity). The alkalinity of water is controlled by the sum of the titratable bases. It is mostly taken as an indication of the concentration of carbonate, bicarbonate and hydroxide, but may include contributions from borate, phosphates, silicates and other basic compounds. Waters of low alkalinity (< 24 ml l^{-1} as $CaCO_3$) have a low buffering capacity and can, therefore, be susceptible to alterations in pH, for example from atmospheric, acidic deposition. Alkalinity is determined by titration. The amount of strong acid needed to lower the pH of a sample to 8.3 gives the free alkalinity, and to pH 4 gives the total alkalinity (see also sections 3.3.10 and 3.6.5).

Ideally, pH should be determined *in situ,* or immediately after the sample is taken, as so many natural factors can influence it. Accurate measurement of pH is usually undertaken electrometrically with a glass electrode, many of which are suitable for field use and for continuous measurement and recording. A rough indication of pH can be obtained colorimetrically with indicator dyes. As pH is temperature dependent, the water temperature must also be measured in order to determine accurately the pH. If field measurement is not possible, samples must be transported to the laboratory in completely full, tightly stoppered bottles with no preservatives added.

3.3.8. Redox potential

The redox potential (Eh) characterises the oxidation-reduction state of natural waters. Ions of the same element but different oxidation states form the redox-system which is characterised by a certain value. Organic compounds can also form redox-systems. The co-existence of a number of such systems leads to an equilibrium which determines the redox-state of the water and is, in turn, characterised by the Eh value. Oxygen, iron and sulphur, as well as some organic systems are the most influential in determining Eh. For example, Eh values increase and may reach + 700 mV when dissolved oxygen concentrations increase. The presence of hydrogen sulphide is usually associated with a sharp decrease in Eh (down to - 100 mV or more) and is evidence of reducing conditions.

The Eh may vary in natural waters from - 500 mV to + 700 mV. Surface waters and groundwaters containing dissolved oxygen are usually characterised by a range of Eh values between + 100 mV and + 500 mV. The Eh of mineral waters connected with oil deposits is significantly lower than zero and may even reach the limit value of - 500 mV.

Redox potential is determined potentiometrically and may be measured *in situ* in the field. Considerable difficulty has been experienced by many workers in obtaining reliable Eh measurements. Therefore, the results and interpretation of any Eh measurements should be treated with caution. As Eh depends on the gas content of the water it can be very variable when the water is in contact with air. Therefore, determination of Eh should be made immediately after sampling whenever *in situ* determination is not possible, and for groundwater it is recommended that Eh is measured “in-line” in the flowing discharge of a pump.

3.3.9. Dissolved oxygen

Oxygen is essential to all forms of aquatic life, including those organisms responsible for the self-purification processes in natural waters. The oxygen content of natural waters varies with temperature, salinity, turbulence, the photosynthetic activity of algae and plants, and atmospheric pressure. The solubility of oxygen decreases as temperature and salinity increase. In fresh-waters dissolved oxygen (DO) at sea level ranges from 15 mg l^{-1} at 0° C to 8 mg l^{-1} at 25° C. Concentrations in unpolluted waters are usually close to, but less than, 10 mg l^{-1}. Dissolved oxygen can also be expressed in terms of percentage saturation, and levels less than 80 per cent saturation in drinking water can usually be detected by consumers as a result of poor odour and taste.

Variations in DO can occur seasonally, or even over 24 hour periods, in relation to temperature and biological activity (i.e. photosynthesis and respiration) (see Figures 6.19 and 6.20). Biological respiration, including that related to decomposition processes, reduces DO concentrations. In still waters, pockets of high and low concentrations of dissolved oxygen can occur depending on the rates of biological processes (see Figure 7.8). Waste discharges high in organic matter and nutrients can lead to decreases in DO concentrations as a result of the increased microbial activity (respiration) occurring during the degradation of the organic matter (see Figures 6.17 and 6.20B). In severe cases of reduced oxygen concentrations (whether natural or man-made), anaerobic conditions can occur (i.e. 0 mg l^{-1} of oxygen), particularly close to the sediment-water interface as a result of decaying, sedimenting material.

Determination of DO concentrations is a fundamental part of a water quality assessment since oxygen is involved in, or influences, nearly all chemical and biological processes within water bodies. Concentrations below 5 mg l^{-1} may adversely affect the functioning and survival of biological communities and below 2 mg l^{-1} may lead to the death of most fish. The measurement of DO can be used to indicate the degree of pollution by organic matter, the destruction of organic substances and the level of self-purification of the water. Its determination is also used in the measurement of biochemical oxygen demand (BOD) (see section 3.5.3).

Dissolved oxygen is of much more limited use as an indicator of pollution in groundwater, and is not useful for evaluating the use of groundwater for normal purposes. In addition, the determination of DO in groundwater requires special equipment and it has not, therefore, been widely carried out. Nevertheless, measurement of DO is critical to the scientific understanding of the potential for chemical and biochemical processes in groundwater. Water that enters groundwater systems as recharge can be expected to contain oxygen at concentrations similar to those of surface water in contact with the atmosphere. Organic matter or oxidisable minerals present in some aquifers rapidly deplete the dissolved oxygen. Therefore, in aquifers where organic materials are less plentiful, groundwater containing measurable concentrations of DO (2-5 mg l^{-1}) can be found.

There are two principal methods for determination of dissolved oxygen. The older, titration method (often called the Winkler method) involves the chemical fixation of the oxygen in a water sample collected in an air-tight bottle. Fixation is carried out in the field and the analysis, by titration, is carried out in the laboratory. The method is time-consuming but can give a high degree of precision and accuracy. It is suitable for most kinds of water and enables samples to be taken and stored. The alternative membrane-electrode, or oxygen probe, method is quick and can be used *in situ* or for continuous monitoring, although a high degree of accuracy may be difficult to maintain.

Samples taken for analysis by titration must be taken with great care to ensure no air bubbles are trapped in the bottle, which must be filled to overflowing and stoppered. The necessary reagents must be added for oxygen fixation immediately the sample is taken and the bottles must be protected from sunlight until the determination is carried out, which should be as soon as possible. Regardless of the analytical method, the water temperature must be measured at the time of sampling.

3.3.10. Carbon dioxide

Carbon dioxide (CO_2) is highly soluble in water and atmospheric CO_2 is absorbed at the air-water interface. In addition, CO_2 is produced within water bodies by the respiration of aquatic biota, during aerobic and anaerobic heterotrophic decomposition of suspended and sedimented organic matter. Carbon dioxide dissolved in natural water is part of an equilibrium involving bicarbonate and carbonate ions (see section 3.6.5). The concentrations of these forms are dependent to some extent on the pH, as indicated in Figure 3.1.

Free CO_2 is that component in gaseous equilibrium with the atmosphere, whereas total CO_2 is the sum of all inorganic forms of carbon dioxide, i.e. CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}. Both CO_2 and HCO_3^- can be incorporated into organic carbon by autotrophic

organisms. Free CO_2 comprises the concentrations of CO_2 plus H_2CO_3, although the latter carbonate form is minimal in most surface waters as they rarely exceed pH 9. At high concentrations of free carbonic acid (pH 4.5 or lower), water becomes corrosive to metals and concrete as a result of the formation of soluble bicarbonates. The ability to affect the calcium carbonate component of concrete has led to the term aggressive carbonic acid or aggressive CO_2, which is also termed free CO_2.

Determination of free CO_2 is usually by titration methods and total CO_2 by calculation from pH and alkalinity estimates. The latter method is subject to some interferences and can be rather inaccurate.

Table 3.3. Conversion factors for various national grades of water hardness

		mmol l^{-1}	**Germany °DH**	**UK °clark**	**France degree F**	**USA ppm**
	mmol l^{-1}	1	5.61	7.02	10	100
Germany	°DK	0.178	1	1.25	1.78	17.8
UK	°Clark	0.143	0.80	1	1.43	14.3
France	degree F	0.1	0.56	0.70	1	10
USA	ppm	0.01	0.056	0.07	0.1	1

Source: ISO, 1984

3.3.11. Hardness

The hardness of natural waters depends mainly on the presence of dissolved calcium and magnesium salts. The total content of these salts is known as general hardness, which can be further divided into carbonate hardness (determined by concentrations of calcium and magnesium hydrocarbonates), and non-carbonate hardness (determined by calcium and magnesium salts of strong acids). Hydrocarbonates are transformed during the boiling of water into carbonates, which usually precipitate. Therefore, carbonate hardness is also known as temporary or removed, whereas the hardness remaining in the water after boiling is called constant. Different countries have different hardness units as indicated in Table 3.3.

Hardness may vary over a wide range. Calcium hardness is usually prevalent (up to 70 per cent), although in some cases magnesium hardness can reach 50-60 per cent. Seasonal variations of river water hardness often occur, reaching the highest values during low flow conditions and the lowest values during floods. Groundwater hardness is, however, less variable. Where there are specific requirements for water hardness in relation to water use it is usually with respect to the properties of the cations forming the hardness.

Samples for hardness determination must be filtered but not preserved. If during storage a calcium carbonate sediment appears, it must be dissolved with a small volume of hydrochloric acid (1:1) after decanting the clear liquid above the sediment. General hardness is usually determined by EDTA complexometric titration. Depending on the indicator used, either general hardness (using eriochrome black T) or calcium hardness (using murexide) can be determined. Magnesium hardness is calculated from the difference between the two determinations. Carbonate hardness is determined by acid-

base titration. Hardness may also be determined from the sum of the divalent ions analysed individually (e.g. by atomic absorption spectrophotometry).

3.3.12. Chlorophyll

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

In waters with little input of sediment from the catchment, or with little re-suspension, chlorophyll can give an approximate indication of the quantity of material suspended in the water column. The growth of planktonic algae in a water body is related to the presence of nutrients (principally nitrates and phosphates), temperature and light. Therefore, concentrations of chlorophyll fluctuate seasonally and even daily, or with water depth, depending on environmental conditions. Water bodies with low levels of nutrients (e.g. oligotrophic lakes) have low levels of chlorophyll (< 2.5 µg l^{-1}) whereas waters with high nutrient contents (especially those classed as eutrophic) have high levels of chlorophyll (5-140 µg l^{-1}), although levels in excess of 300 µg l^{-1} also occur.

Chlorophyll fluoresces red when excited by blue light and this property can be used to measure chlorophyll levels and indicate algal biomass. Direct, and continuous, measurement of chlorophyll fluorescence can be made with a fluorimeter which can be used *in situ* by pumping water through it or, for some specially designed instruments, by lowering it into the water. Samples taken for chlorophyll analysis in the laboratory should be collected in polythene bottles and 0.1 to 0.2 ml of magnesium carbonate suspension added immediately as a preservative. Samples should also be filtered immediately although they can be stored in a cool dark place for up to 8 hours. However, once filtered through a glass fibre (GF/C grade) filter, the filter can be stored frozen for a short period prior to analysis. The chlorophyll pigments are solvent-extracted and measured spectrophotometrically using one of the methods described by Strickland and Parsons (1972). The most common determination is for chlorophyll *a,* although some methods allow for the combined measurements of chlorophylls *a, b* and *c*. The presence of chlorophyll degradation products, such as phaeophytin, can interfere with the estimate of chlorophyll concentrations in the solvent extract. This can be overcome by reading the optical density before and after acidification of the extract, using the method based on Lorenzen (1967). A rough estimate of phytoplankton organic carbon can be obtained from a measurement of total pigments (i.e. chlorophyll *a* + phaeopigments). The minimum organic carbon present (in mg l^{-1}) is approximately equal to 30 times the total pigments (in mg l^{-1}), although this relationship has only been tested on western European rivers (Dessery *et al.,* 1984).

3.4. Nutrients

3.4.1. Nitrogen compounds

Nitrogen is essential for living organisms as an important constituent of proteins, including genetic material. Plants and micro-organisms convert inorganic nitrogen to

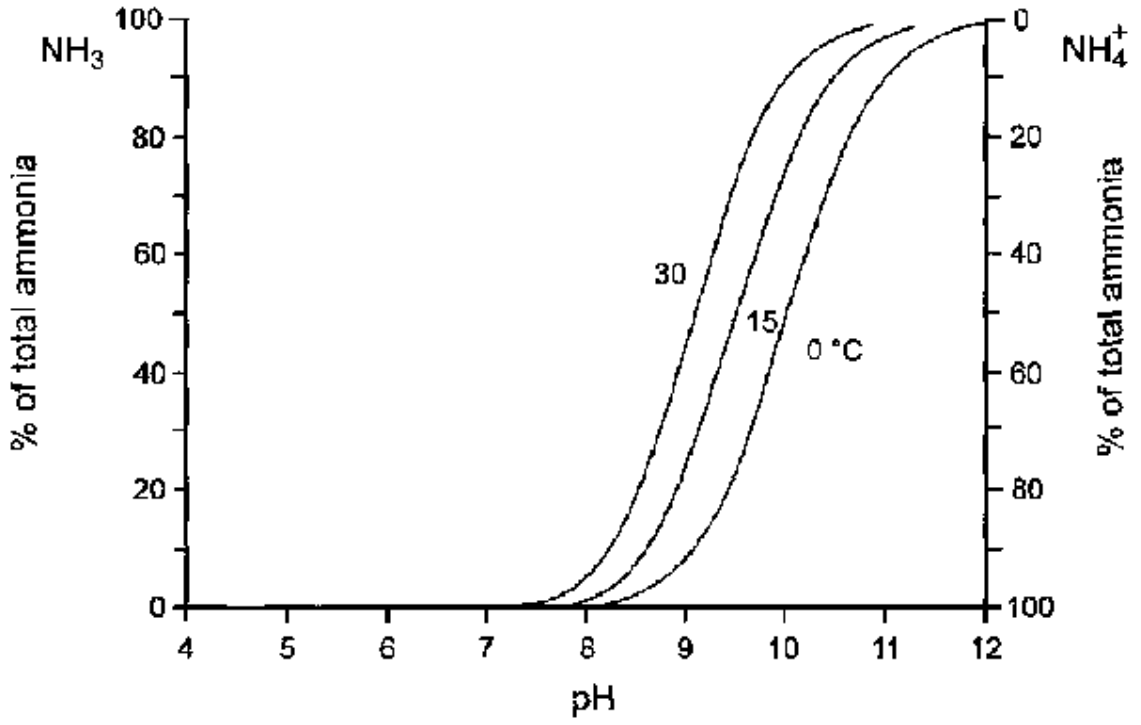
organic forms. In the environment, inorganic nitrogen occurs in a range of oxidation states as nitrate (NO_3^-) and nitrite (NO_2^-), the ammonium ion (NH_4^+) and molecular nitrogen (N_2). It undergoes biological and non-biological transformations in the environment as part of the nitrogen cycle. The major non-biological processes involve phase transformations such as volatilisation, sorption and sedimentation. The biological transformations consist of: a) assimilation of inorganic forms (ammonia and nitrate) by plants and micro-organisms to form organic nitrogen e.g. amino acids, b) reduction of nitrogen gas to ammonia and organic nitrogen by micro-organisms, c) complex heterotrophic conversions from one organism to another, d) oxidation of ammonia to nitrate and nitrite (nitrification), e) ammonification of organic nitrogen to produce ammonia during the decomposition of organic matter, and f) bacterial reduction of nitrate to nitrous oxide (N_2O) and molecular nitrogen (N_2) under anoxic conditions (denitrification). For a better understanding of the nitrogen cycle it is strongly recommended that all nitrogen species are reported in moles per litre or as mg l^{-1} of nitrogen (e.g. NO_3-N, NH_4-N), rather than as mg l^{-1} of NO_3^- or NH_4^+.

Ammonia

Ammonia occurs naturally in water bodies arising from the breakdown of nitrogenous organic and inorganic matter in soil and water, excretion by biota, reduction of the nitrogen gas in water by micro-organisms and from gas exchange with the atmosphere. It is also discharged into water bodies by some industrial processes (e.g. ammonia-based pulp and paper production) and also as a component of municipal or community waste. At certain pH levels, high concentrations of ammonia (NH_3) are toxic to aquatic life and, therefore, detrimental to the ecological balance of water bodies.

In aqueous solution, un-ionised ammonia exists in equilibrium with the ammonium ion. Total ammonia is the sum of these two forms. Ammonia also forms complexes with several metal ions and may be adsorbed onto colloidal particles, suspended sediments and bed sediments. It may also be exchanged between sediments and the overlying water. The concentration of un-ionised ammonia is dependent on the temperature, pH and total ammonia concentration. The change in percentage of the two forms at different pH values is shown in Figure 3.2. Substantial losses of ammonia can occur via volatilisation with increasing pH.

Figure 3.2. The general relationship between the percentage of un-ionised and free ammonia and varying pH in pure freshwaters



Unpolluted waters contain small amounts of ammonia and ammonia compounds, usually <0.1 mg l^{-1} as nitrogen. Total ammonia concentrations measured in surface waters are typically less than 0.2 mg l^{-1} N but may reach 2-3 mg l^{-1} N. Higher concentrations could be an indication of organic pollution such as from domestic sewage, industrial waste and fertiliser run-off. Ammonia is, therefore, a useful indicator of organic pollution. Natural seasonal fluctuations also occur as a result of the death and decay of aquatic organisms, particularly phytoplankton and bacteria in nutritionally rich waters. High ammonia concentrations may also be found in the bottom waters of lakes which have become anoxic.

Samples intended for the detection of ammonia should be analysed within 24 hours. If this is not possible the sample can be deep frozen or preserved with 0.8 ml of sulphuric acid (H_2SO_4) for each litre of sample and then stored at 4° C. Prior to analysis any acid used as a preservative should be neutralised. There are many methods available for measuring ammonia ions. The simplest, which are suitable for waters with little or no pollution, are colorimetric methods using Nessler's reagent or the phenate method. For high concentrations of ammonia, such as occur in wastewaters, a distillation and titration method is more appropriate. Total ammonia nitrogen is also determined as part of the Kjeldahl method (see below).

Nitrate and nitrite

The nitrate ion (NO_3^-) is the common form of combined nitrogen found in natural waters. It may be biochemically reduced to nitrite (NO_2^-) by denitrification processes, usually

under anaerobic conditions. The nitrite ion is rapidly oxidised to nitrate. Natural sources of nitrate to surface waters include igneous rocks, land drainage and plant and animal debris. Nitrate is an essential nutrient for aquatic plants and seasonal fluctuations can be caused by plant growth and decay. Natural concentrations, which seldom exceed 0.1 mg l^{-1} NO_3-N, may be enhanced by municipal and industrial waste-waters, including leachates from waste disposal sites and sanitary landfills. In rural and suburban areas, the use of inorganic nitrate fertilisers can be a significant source.

When influenced by human activities, surface waters can have nitrate concentrations up to 5 mg l^{-1} NO_3-N, but often less than 1 mg l^{-1} NO_3-N. Concentrations in excess of 5 mg l^{-1} NO_3-N usually indicate pollution by human or animal waste, or fertiliser run-off. In cases of extreme pollution, concentrations may reach 200 mg l^{-1} NO_3-N. The World Health Organization (WHO) recommended maximum limit for NO_3^- in drinking water is 50 mg l^{-1} (or 11.3 mg l^{-1} as NO_3-N) (Table 3.4), and waters with higher concentrations can represent a significant health risk. In lakes, concentrations of nitrate in excess of 0.2 mg l^{-1} NO_3-N tend to stimulate algal growth and indicate possible eutrophic conditions.

Nitrate occurs naturally in groundwaters as a result of soil leaching but in areas of high nitrogen fertiliser application it may reach very high concentrations (~500 mg l^{-1} NO_3-N). In some areas, sharp increases in nitrate concentrations in groundwaters over the last 20 or 30 years have been related to increased fertiliser applications, especially in many of the traditional agricultural regions of Europe (Hagebro *et al.,* 1983; Roberts and Marsh, 1987). Increased fertiliser application is not, however, the only source of nitrate leaching to groundwater. Nitrate leaching from unfertilised grassland or natural vegetation is normally minimal, although soils in such areas contain sufficient organic matter to be a large potential source of nitrate (due to the activity of nitrifying bacteria in the soil). On clearing and ploughing for cultivation, the increased soil aeration that occurs enhances the action of nitrifying bacteria, and the production of soil nitrate.

Table 3.4. Examples of maximum allowable concentrations of selected water quality variables for different uses

Use	**Drinking water**					**Fisheries and aquatic life**		
Variable	**WHO[1]**	**EU**	**Canada**	**USA**	**Russia[2]**	**EU**	**Canada[1]**	**Russia**
Colour (TCU)	15	20 mg l^{-1} Pt-Co	15	15	20			
Total dissolved solids (mg l^{-1})	1,000		500	500	1,000			
Total suspended solids (mg l^{-1})						25	inc. of 10 or 10%[3]	
Turbidity (NTU)	5	4 JTU	5	0.5-1.0				
pH	< 8.0[4]	6.5[1]-8.5[1]	6.5-8.5	6.5-8.5	6.0-9.0	6.0-9.0	6.5-9.0	
Dissolved oxygen (mg l^{-1})					4.0	5.0-9.0	5.0-9.5	4.0[5]-6.0
Ammoniacal nitrogen					2.0	0.005-	1.37-2.2[6,7]	0.05

(mg l^{-1})						0.025		
Ammonium (mg l^{-1})		0,5			2.0	0.04-1.0		0.5
Nitrate as N (mg l^{-1})			10.0	10.0				
Nitrate (mg l^{-1})	50	50			45			40
Nitrite as N (mg l^{-1})			1.0	1.0				
Nitrite (mg l^{-1})	3(P)	0.1			3.0	0.01-0.03	0.06	0.08
Phosphorus (mg l^{-1})		5.0						
BOD (mg l^{-1} O_2)					3.0	3.0-6.0		3
Sodium (mg l^{-1})	200	150						120
Chloride (mg l^{-1})	250	25[1]	250	250	350			300
Chlorine (mg l^{-1})	5						0.002	
Sulphate (mg l^{-1})	250	250	500	250	500			100
Sulphide (mg l^{-1})			0.05					
Fluoride (mg l^{-1})	1.5	1.5	1.5	2.0	< 1.5			0.75
Boron (mg l^{-1})	0.3	1.0[1]	5.0		0.3			
Cyanide (mg l^{-1})	0.07	0.05	0.2	0.2 (PP)	0.07		0.005	0.05
Trace elements								
Aluminium (mg l^{-1})	0.2	0.2			0.5		0.005-0.1[7]	
Arsenic (mg l^{-1})	0.01 (P)	0.05	0.05	0.05	0.01		0.05	
Barium (mg l^{-1})	0.7	0.1[1]	1.0	2.0	0.7			
Cadmium (mg l^{-1})	0.003	0.005	0.005	0.005	0.003		0.0002-0.0018[8]	0.005
Chromium (mg l^{-1})	0.05 (P)	0.05	0.05	0.1	0.05		0.02-0.002	0.02-0.005
Cobalt (mg l^{-1})					0.1			0.01
Copper (mg l^{-1})	2(P)	0.1[1]-3.0[1]	1.0	1	2.0	0.005-0.112[8,9]	0.002-0.004[8]	0.001
Iron (mg l^{-1})	0.3	0.2	0.3	0.3	0.3		0.3	0.1
Lead (mg l^{-1})	0.01	0.05	0.05	0.015	0.01		0.001-0.007[8]	0.1
Manganese (mg l^{-1})	0.5(P)	0.05	0.05	0.05	0.5			0.01
Mercury (mg l^{-1})	0.001	0.001	0.001	0.002	0.001		0.0001	0.00001
Nickel (mg l^{-1})	0.02	0.05			0.02		0.025-0.15[8]	0.01
Selenium (mg l^{-1})	0.01	0.01	0.01	0.05	0.01		0.001	0.0016
Zinc(mg l^{-1})	3	0.1[1]-5.0[1]	5.0	5	5.0	0.03-2.0[8,10]	0.03	0.01
Organic contaminants[11]								
Oil and petroleum								

products (mg l^{-1})		0.01			0.1			0.05
Total pesticides (µg l^{-1})		0.5	100					
Aldrin & dieldrin (µg l^{-1})	0.03		0.7				4 ng l^{-1} dieldrin	
DDT (µg l^{-1})	2		30.0		2.0		1 ng l^{-1}	
Lindane (µg l^{-1})	2		4.0	0.2	2.0			
Methoxychlor (µg l^{-1})	20		100	40				
Benzene (µg l^{-1})	10			5			300	
Pentachlorophenol (µg l^{-1})	9(P)			10	10			
Phenols (µg l^{-1})		0.5	2		1.0		1.0	1.0
Detergents (mg l^{-1})		0.2		0.5[12]	0.5			0.1
Microbiological variables								
Faecal coliforms (*E. coli*) (No. per 100 ml)	0	0	0		0			
Total coliforms (No. per 100 ml)	0		10[13]	1	0.3			

WHO World Health Organization
EU European Union
BOD Biochemical oxygen demand
TCU True colour units
NTU Nephelometric turbidity units
(P) Provisional value
(PP) Proposed value

[1] Guideline value
[2] Some values not yet adopted but already applied
[3] i.e. above background concentrations of ≤ 100.0 mg l^{-1} or > 100 mg l^{-1} respectively
[4] For effective disinfection with chlorine
[5] Lower level acceptable under ice cover
[6] Total ammonia
[7] Depending on pH
[8] Depending on hardness
[9] Dissolved only
[10] Total zinc
[11] For some groups values are also set for individual compounds
[12] Foaming agents
[13] For a single sample

Sources: Environment Canada, 1987 CEC, 1978, 1980 Committee for Fisheries, 1993 Gray, 1994 WHO, 1993

Nitrite concentrations in freshwaters are usually very low, 0.001 mg l^{-1} NO_2-N, and rarely higher than 1 mg l^{-1} NO_2-N. High nitrite concentrations are generally indicative of industrial effluents and are often associated with unsatisfactory microbiological quality of water.

Determination of nitrate plus nitrite in surface waters gives a general indication of the nutrient status and level of organic pollution. Consequently, these species are included in most basic water quality surveys and multipurpose or background monitoring programmes, and are specifically included in programmes monitoring the impact of organic or relevant industrial inputs. As a result of the potential health risk of high levels of nitrate, it is also measured in drinking water sources. However, as little nitrate is removed during the normal processes for drinking water treatment, the treated drinking water should also be analysed when nitrate concentrations are high in the source water.

Samples taken for the determination of nitrate and/or nitrite should be collected in glass or polyethylene bottles and filtered and analysed immediately. If this is not possible, 2-4 ml of chloroform per litre can be added to the sample to retard bacterial decomposition. The sample can be cooled and then stored at 3-4° C. As determination of nitrate is difficult, due to interferences from other substances present in the water, the precise choice of method may vary according to the expected concentration of nitrate as N. Alternatively, one portion of the sample can be chemically analysed for total inorganic nitrogen and the other for nitrite, and the nitrate concentration obtained from the difference between the two values. Nitrite concentrations can be determined using spectrophotometric methods. Some simple field determinations, of limited accuracy, can be made using colorimetric comparator methods available as kits.

Organic nitrogen

Organic nitrogen consists mainly of protein substances (e.g. amino acids, nucleic acids and urine) and the product of their biochemical transformations (e.g. humic acids and fulvic acids). Organic nitrogen is naturally subject to the seasonal fluctuations of the biological community because it is mainly formed in water by phytoplankton and bacteria, and cycled within the food chain. Increased concentrations of organic nitrogen could indicate pollution of a water body.

Organic nitrogen is usually determined using the Kjeldahl method which gives total ammonia nitrogen plus total organic nitrogen (Kjeldahl N). The difference between the total nitrogen and the inorganic forms gives the total organic nitrogen content. Samples must be unfiltered and analysed within 24 hours, since organic nitrogen is rapidly converted to ammonia. This process can be retarded if necessary by the addition of 2-4 ml of chloroform or approximately 0.8 ml of concentrated H_2SO_4 per litre of sample. Storage should be at 2-4° C, and when this is necessary, the condition and duration of preservation should be stated with the results. Photochemical methods can also be used in place of the Kjeldahl method. These methods oxidise all organic nitrogen (as well as ammonia) to nitrates and nitrites and, therefore, the measurements of these must already have been carried out on the sample beforehand. If samples are filtered total dissolved nitrogen is determined instead of total organic nitrogen.

3.4.2. Phosphorus compounds

Phosphorus is an essential nutrient for living organisms and exists in water bodies as both dissolved and particulate species. It is generally the limiting nutrient for algal growth and, therefore, controls the primary productivity of a water body. Artificial increases in concentrations due to human activities are the principal cause of eutrophication (see Chapter 7).

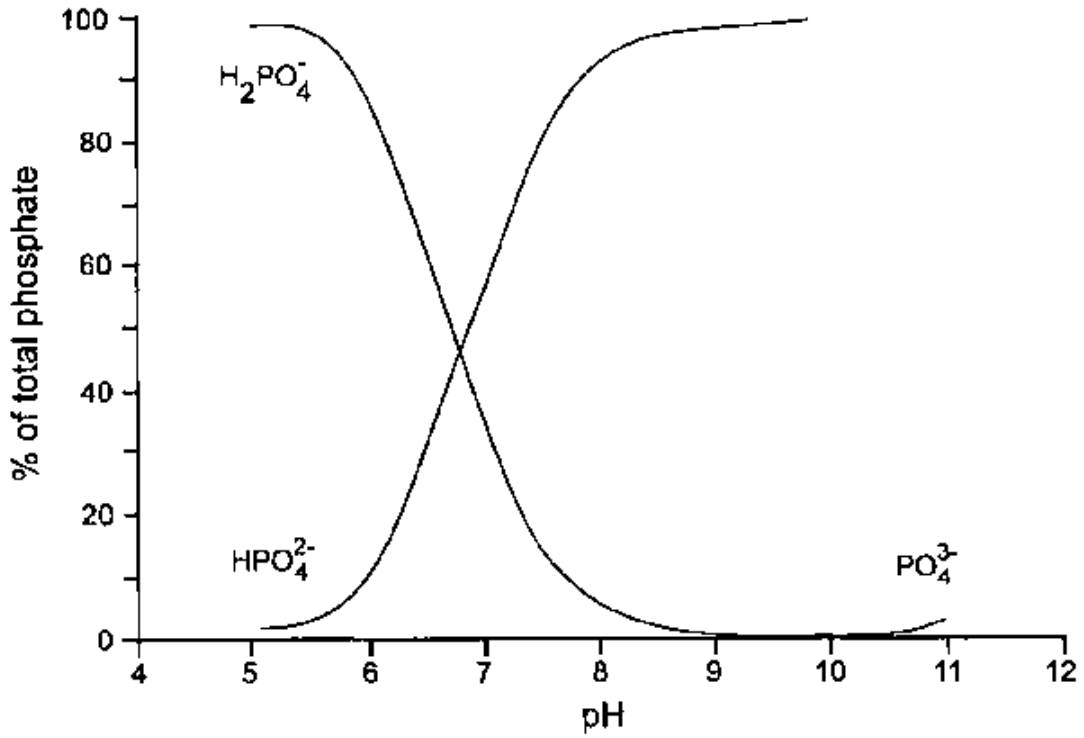
In natural waters and in wastewaters, phosphorus occurs mostly as dissolved orthophosphates and polyphosphates, and organically bound phosphates. Changes between these forms occur continuously due to decomposition and synthesis of organically bound forms and oxidised inorganic forms. The equilibrium of the different forms of phosphate that occur at different pH values in pure water is shown in Figure 3.3. It is recommended that phosphate concentrations are expressed as phosphorus, i.e. mg l^{-1} PO_4-P (and not as mg l^{-1} PO_4^{3-}).

Natural sources of phosphorus are mainly the weathering of phosphorus-bearing rocks and the decomposition of organic matter. Domestic waste-waters (particularly those containing detergents), industrial effluents and fertiliser run-off contribute to elevated levels in surface waters. Phosphorus associated with organic and mineral constituents of sediments in water bodies can also be mobilised by bacteria and released to the water column.

Phosphorus is rarely found in high concentrations in freshwaters as it is actively taken up by plants. As a result there can be considerable seasonal fluctuations in concentrations in surface waters. In most natural surface waters, phosphorus ranges from 0.005 to 0.020 mg l^{-1} PO_4-P. Concentrations as low as 0.001 mg l^{-1} PO_4-P may be found in some pristine waters and as high as 200 mg l^{-1} PO_4-P in some enclosed saline waters. Average groundwater levels are about 0.02 mg l^{-1} PO_4-P.

As phosphorus is an essential component of the biological cycle in water bodies, it is often included in basic water quality surveys or background monitoring programmes. High concentrations of phosphates can indicate the presence of pollution and are largely responsible for eutrophic conditions. The management of a lake or reservoir, particularly for drinking water supply, requires a knowledge of the levels of phosphate in order to help interpret the rates of algal growth.

Figure 3.3. The equilibrium of different forms of phosphate in relation to the pH of pure freshwaters



Phosphorus concentrations are usually determined as orthophosphates, total inorganic phosphate or total phosphorus (organically combined phosphorus and all phosphates). The dissolved forms of phosphorus are measured after filtering the sample through a pre-washed 0.45 µm pore diameter membrane filter. Particulate concentrations can be deduced by the difference between total and dissolved concentrations. Phosphorus is readily adsorbed onto the surface of sample containers and, therefore, containers should be rinsed thoroughly with the sample before use. Samples for phosphate analysis can be preserved with chloroform and stored at 2-4° C for up to 24 hours. Samples for total phosphorus determinations can be stored in a glass flask with a tightly fitting glass stopper, provided 1 ml of 30 per cent sulphuric acid is added per 100 ml of sample. For dissolved phosphorus, it is important that samples are filtered as soon as possible after collection. Determination of phosphate involves conversion to orthophosphate which is then measured colorimetrically.

3.5. Organic matter

Most freshwaters contain organic matter which can be measured as total organic carbon (TOC). For comparative purposes an indication of the amount of organic matter present can be obtained by measuring related properties, principally the biochemical oxygen demand (BOD) or the chemical oxygen demand (COD). The COD usually includes all, or most, of the BOD as well as some other chemical demands. In most samples, COD > BOD > TOC. However, in some situations this relationship may not be true, such as when the sample contains toxic substances (see section 3.5.3).

3.5.1. Total organic carbon

Organic carbon in freshwaters arises from living material (directly from plant photosynthesis or indirectly from terrestrial organic matter) and also as a constituent of many waste materials and effluents. Consequently, the total organic matter in the water can be a useful indication of the degree of pollution, particularly when concentrations can be compared upstream and downstream of potential sources of pollution, such as sewage or industrial discharges or urban areas. In surface waters, TOC concentrations are generally less than 10 mg l^{-1}, and in groundwater less than 2 mg l^{-1}, unless the water receives municipal or industrial wastes, or is highly coloured due to natural organic material, as in swamps. In such situations, TOC concentrations may exceed 100 mg l^{-1} (TOC concentrations in municipal wastewaters range from 10 to > 100 mg l^{-1}, depending on the level of wastewater treatment). Total organic carbon consists of dissolved and particulate material and is, therefore, affected by fluctuations in suspended solids, which can be quite pronounced in rivers. The dissolved and particulate organic carbon (DOC and POC respectively) can be determined separately after filtering the sample through a glass fibre filter (approximately 0.7 µm pore diameter), and this is recommended for river studies. In most surface waters, DOC levels exceed POC levels and are in the range 1-20 mg l^{-1}. During river floods, and throughout the year in many turbid rivers, POC is the most abundant form (see Table 6.3).

Total organic carbon is determined without filtration of the sample. Samples for TOC determination should be stored in dark glass bottles, with minimum exposure to light or air, at 3-4° C for no more than seven days prior to analysis. Alternatively, samples can be acidified with sulphuric acid to pH 2 or less.

There are various methods available for determining organic carbon depending on the type of sample to be analysed. Methods are based on the principle of oxidation of the carbon in the sample to carbon dioxide (e.g. by combustion, chemical reaction or ultra violet irradiation) which is then determined by one of several methods (e.g. volumetric determination, thermal conductivity or specific CO_2 electrode).

3.5.2. Chemical oxygen demand

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant, such as dichromate. The COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and in the effluents from sewage and industrial plants. The test for COD is non-specific, in that it does not identify the oxidisable material or differentiate between the organic and inorganic material present. Similarly, it does not indicate the total organic carbon present since some organic compounds are not oxidised by the dichromate method whereas some inorganic compounds are oxidised. Nevertheless, COD is a useful, rapidly measured, variable for many industrial wastes and has been in use for several decades.

The concentrations of COD observed in surface waters range from 20 mg l^{-1} O_2 or less in unpolluted waters to greater than 200 mg l^{-1} O_2 in waters receiving effluents. Industrial wastewaters may have COD values ranging from 100 mg l^{-1} O_2 to 60,000 mg l^{-1} O_2.

Samples for COD analysis should be collected in bottles which do not release organic substances into the water, such as glass-stoppered glass bottles. Ideally samples should be analysed immediately, or if unpolluted, within 24 hours provided they are stored cold. If analysis cannot be carried out immediately, the samples should be preserved with sulphuric acid. For prolonged storage samples should be deep frozen. If appropriate, samples can be filtered prior to analysis using glass fibre filters. Unfiltered samples containing settleable solids should be homogenised prior to sub-sampling. The standard method for measurement of COD is oxidation of the sample with potassium dichromate in a sulphuric acid solution (although other oxidants can be used which may have different oxidation characteristics) followed by a titration. It is extremely important that the same method is followed each time during a series of measurements so that the results are comparable.

3.5.3. Biochemical oxygen demand

The biochemical oxygen demand (BOD) is an approximate measure of the amount of biochemically degradable organic matter present in a water sample. It is defined by the amount of oxygen required for the aerobic micro-organisms present in the sample to oxidise the organic matter to a stable inorganic form. The method is subject to various complicating factors such as the oxygen demand resulting from the respiration of algae in the sample and the possible oxidation of ammonia (if nitrifying bacteria are also present). The presence of toxic substances in a sample may affect microbial activity leading to a reduction in the measured BOD. The conditions in a BOD bottle usually differ from those in a river or lake. Therefore, interpretation of BOD results and their implications must be done with great care and by experienced personnel. Further discussion of the BOD test, together with case history results, is given in Velz (1984).

Standardised laboratory procedures are used to determine BOD by measuring the amount of oxygen consumed after incubating the sample in the dark at a specified temperature, which is usually 20° C, for a specific period of time, usually five days. This gives rise to the commonly used term "BOD_5". The oxygen consumption is determined from the difference between the dissolved oxygen concentrations in the sample before and after the incubation period. If the concentration of organic material in the samples is very high, samples may require dilution with distilled water prior to incubation so that the oxygen is not totally depleted.

As noted above, BOD measurements are usually lower than COD measurements. Unpolluted waters typically have BOD values of 2 mg l^{-1} O_3 or less, whereas those receiving wastewaters may have values up to 10 mg l^{-1} O_2 or more, particularly near to the point of wastewater discharge. Raw sewage has a BOD of about 600 mg l^{-1} O_2, whereas treated sewage effluents have BOD values ranging from 20 to 100 mg l^{-1} O_2 depending on the level of treatment applied. Industrial wastes may have BOD values up to 25,000 mg l^{-1} O_2.

Water samples collected for BOD measurement must not contain any added preservatives and must be stored in glass bottles. Ideally the sample should be tested immediately since any form of storage at room temperature can cause changes in the BOD (increase or decrease depending on the character of the sample) by as much as 40 per cent. Storage should be at 5° C and only when absolutely necessary.

3.5.4 Humic and fulvic acids

Organic matter arising from living organisms makes an important contribution to the natural quality of surface waters. The composition of this organic matter is extremely diverse. Natural organic compounds are not usually toxic, but exert major controlling effects on the hydrochemical and biochemical processes in a water body. Some natural organic compounds significantly affect the quality of water for certain uses, especially those which depend on organoleptic properties (taste and smell). During chlorination for drinking water disinfection, humic and fulvic acids act as precursor substances in the formation of tribalomethanes such as chloroform. In addition, substances included in aquatic humus determine the speciation of heavy metals and some other pollutants because of their high complexing ability. As a result, humic substances affect the toxicity and mobility of metal complexes. Therefore, measurement of the concentrations of these substances can be important for determining anthropogenic impacts on water bodies.

Humus is formed by the chemical and biochemical decomposition of vegetative residues and from the synthetic activity of micro-organisms. Humus enters water bodies from the soil and from peat bogs, or it can be formed directly within water bodies as a result of biochemical transformations. It is operationally separated into fulvic and humic acid fractions, each being an aggregate of many organic compounds of different masses. Fulvic acid has molecular masses mostly in the range 300-5,000 whereas the dominant masses in humic acid exceed 5,000. The relative content of fulvic acid in the dissolved humic substances present in freshwaters is between 60 and 90 per cent. Humic and fulvic acids are fairly stable (i.e. their BOD is low). However, these substances are chemically oxidisable and, therefore, can readily affect the results of COD determinations.

Fulvic and humic acid concentrations in river and lake waters are highly dependent on the physico-geographical conditions and are usually in the range of tens and hundreds of micrograms of carbon per litre. However, concentrations can reach milligrams of carbon per litre in waters of marshy and woodland areas. In natural conditions fulvic and humic acids can comprise up to 80 per cent of the DOC, which can be used as an approximate estimate of their concentrations.

Samples for fulvic and humic acid determination are not usually filtered or preserved. They can be stored for some months in a refrigerator (3-4° C). Total fulvic and humic acid content can be determined photometrically and their separate determination can be made with spectrophotometric methods.

3.6. Major ions

Major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}) are naturally very variable in surface and groundwaters due to local geological, climatic and geographical conditions (see Tables 6.2, 6.3 and 9.4).

3.6.1. Sodium

All natural waters contain some sodium since sodium salts are highly water soluble and it is one of the most abundant elements on earth. It is found in the ionic form (Na^{+}), and in plant and animal matter (it is an essential element for living organisms). Increased

concentrations in surface waters may arise from sewage and industrial effluents and from the use of salts on roads to control snow and ice. The latter source can also contribute to increased sodium in groundwaters. In coastal areas, sea water intrusion can also result in higher concentrations.

Concentrations of sodium in natural surface waters vary considerably depending on local geological conditions, wastewater discharges and seasonal use of road salt. Values can range from 1 mg l^{-1} or less to 10^5 mg l^{-1} or more in natural brines. The WHO guideline limit for sodium in drinking water is 200 mg l^{-1} (Table 3.4). Many surface waters, including those receiving wastewaters, have concentrations well below 50 mg l^{-1}. However, ground-water concentrations frequently exceed 50 mg l^{-1}.

Sodium is commonly measured where the water is to be used for drinking or agricultural purposes, particularly irrigation. Elevated sodium in certain soil types can degrade soil structure thereby restricting water movement and affecting plant growth. The sodium adsorption ratio (SAR) is used to evaluate the suitability of water for irrigation. The ratio estimates the degree to which sodium will be adsorbed by the soil. High values of SAR imply that the sodium in the irrigation water may replace the calcium and magnesium ions in the soil, potentially causing damage to the soil structure. The SAR for irrigation waters is defined as follows:

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

where the concentrations of sodium, magnesium and calcium are expressed in milliequivalents per litre (meq l^{-1}).

Samples for sodium analysis should be stored in polyethylene bottles to avoid potential leaching from glass containers. Samples should be analysed as soon as possible because prolonged storage in polyethylene containers can lead to evaporation losses through the container walls or lid. Filtration may be necessary if the sample contains solid material. Analysis is best performed using flame atomic emission and absorption.

3.6.2. Potassium

Potassium (as K^+) is found in low concentrations in natural waters since rocks which contain potassium are relatively resistant to weathering. However, potassium salts are widely used in industry and in fertilisers for agriculture and enter freshwaters with industrial discharges and run-off from agricultural land.

Potassium is usually found in the ionic form and the salts are highly soluble. It is readily incorporated into mineral structures and accumulated by aquatic biota as it is an essential nutritional element. Concentrations in natural waters are usually less than 10 mg l^{-1}, whereas concentrations as high as 100 and 25,000 mg l^{-1} can occur in hot springs and brines, respectively.

Samples for potassium analysis should be stored in polyethylene containers to avoid potential contamination as a result of leaching from glass bottles. However, samples

should be analysed as soon as possible as prolonged storage in polyethylene containers can lead to evaporation losses through the container walls or lid. Samples containing solids may require filtration prior to storage. Analysis is best carried out using atomic absorption spectrophotometry as for sodium.

3.6.3. Calcium

Calcium is present in all waters as Ca^{2+} and is readily dissolved from rocks rich in calcium minerals, particularly as carbonates and sulphates, especially limestone and gypsum. The cation is abundant in surface and groundwaters. The salts of calcium, together with those of magnesium, are responsible for the hardness of water (see section 3.3.11). Industrial, as well as water and wastewater treatment, processes also contribute calcium to surface waters. Acidic rainwater can increase the leaching of calcium from soils.

Calcium compounds are stable in water when carbon dioxide is present, but calcium concentrations can fall when calcium carbonate precipitates due to increased water temperature, photosynthetic activity or loss of carbon dioxide due to increases in pressure. Calcium is an essential element for all organisms and is incorporated into the shells of many aquatic invertebrates, as well as the bones of vertebrates. Calcium concentrations in natural waters are typically < 15 mg l^{-1}. For waters associated with carbonate-rich rocks, concentrations may reach 30-100 mg l^{-1}. Salt waters have concentrations of several hundred milligrams per litre or more.

Samples for calcium analysis should be collected in plastic or borosilicate glass bottles without a preservative. They should be analysed immediately, or as soon as possible, after collection and filtration. If any calcium carbonate precipitate forms after filtration and during storage, it must be re-dissolved with hydrochloric or nitric acid and then neutralised before analysis. Acidification of unfiltered waters prior to analysis should be avoided since it causes a dissolution of carbonates, calcite and dolomite. Calcium can be determined by a titrimetric method using EDTA (ethylenediaminetetracetic acid) or by atomic absorption spectrophotometry.

3.6.4. Magnesium

Magnesium is common in natural waters as Mg^{2+}, and along with calcium, is a main contributor to water hardness (see section 3.3.11). Magnesium arises principally from the weathering of rocks containing ferromagnesium minerals and from some carbonate rocks. Magnesium occurs in many organometallic compounds and in organic matter, since it is an essential element for living organisms. Natural concentrations of magnesium in fresh-waters may range from 1 to > 100 mg l^{-1}, depending on the rock types within the catchment. Although magnesium is used in many industrial processes, these contribute relatively little to the total magnesium in surface waters.

Samples for magnesium analysis should be collected in plastic or borosilicate glass containers without preservative. Samples can be analysed using the EDTA titrimetric method or by atomic absorption spectrophotometry. The magnesium concentration in a sample can also be estimated by calculating the difference between the total hardness and the calcium concentration.

3.6.5. Carbonates and bicarbonates

The presence of carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-) influences the hardness and alkalinity of water (see sections 3.3.11 and 3.3.7). The inorganic carbon component (CO_2) arises from the atmosphere (see section 3.3.10) and biological respiration. The weathering of rocks contributes carbonate and bicarbonate salts. In areas of non-carbonate rocks, the HCO_3^- and CO_3^{2-} originate entirely from the atmosphere and soil CO_2, whereas in areas of carbonate rocks, the rock itself contributes approximately 50 per cent of the carbonate and bicarbonate present.

The relative amounts of carbonates, bicarbonates and carbonic acid in pure water are related to the pH as shown in Figure 3.1. As a result of the weathering process, combined with the pH range of surface waters (~6-8.2), bicarbonate is the dominant anion in most surface waters. Carbonate is uncommon in natural surface waters because they rarely exceed pH 9, whereas groundwaters can be more alkaline and may have concentrations of carbonate up to 10 mg l^{-1}. Bicarbonate concentrations in surface waters are usually < 500 mg l^{-1}, and commonly < 25 mg l^{-1}.

The concentration of carbonates and bicarbonates can be calculated from the free and total alkalinity. However, the calculation is valid only for pure water since it assumes that the alkalinity derives only from carbonates and bicarbonates. In some cases, hydroxyl ions are also present, and even unpolluted or mildly polluted waters contain components which affect the calculation.

3.6.6. Chloride

Most chlorine occurs as chloride (Cl^-) in solution. It enters surface waters with the atmospheric deposition of oceanic aerosols, with the weathering of some sedimentary rocks (mostly rock salt deposits) and from industrial and sewage effluents, and agricultural and road run-off. The salting of roads during winter periods can contribute significantly to chloride increases in groundwaters. High concentrations of chloride can make waters unpalatable and, therefore, unfit for drinking or livestock watering.

In pristine freshwaters chloride concentrations are usually lower than 10 mg l^{-1} and sometimes less than 2 mg l^{-1}. Higher concentrations can occur near sewage and other waste outlets, irrigation drains, salt water intrusions, in arid areas and in wet coastal areas. Seasonal fluctuations of chloride concentrations in surface waters can occur where roads are salted in the winter. As chloride is frequently associated with sewage, it is often incorporated into assessments as an indication of possible faecal contamination or as a measure of the extent of the dispersion of sewage discharges in water bodies.

Samples for chloride determination need no preservation or special treatment and can be stored at room temperature. Analysis can be done by standard or potentiometric titration methods. Direct potentiometric determinations can be made with chloride-sensitive electrodes.

3.6.7. Sulphate

Sulphate is naturally present in surface waters as SO_4^{2-}. It arises from the atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate

minerals such as gypsum or sulphide minerals such as pyrite, from sedimentary rocks. It is the stable, oxidised form of sulphur and is readily soluble in water (with the exception of lead, barium and strontium sulphates which precipitate). Industrial discharges and atmospheric precipitation can also add significant amounts of sulphate to surface waters. Sulphate can be used as an oxygen source by bacteria which convert it to hydrogen sulphide (H_2S, HS^-) under anaerobic conditions.

Sulphate concentrations in natural waters are usually between 2 and 80 mg l^{-1}, although they may exceed 1,000 mg l^{-1} near industrial discharges or in arid regions where sulphate minerals, such as gypsum, are present. High concentrations (> 400 mg l^{-1}) may make water unpleasant to drink.

Samples collected in plastic or glass containers can be stored in the refrigerator for up to seven days, although when intended for analysis soon after collection they may be stored at room temperature. Prolonged storage should be avoided, particularly if the sample contains polluted water. Sulphate can be determined gravimetrically after precipitation by barium chloride in hot hydrochloric acid. Other methods are available including a titrimetric method.

3.7. Other inorganic variables

3.7.1. Sulphide

Sulphide enters groundwaters as a result of the decomposition of sulphurous minerals and from volcanic gases. Sulphide formation in surface waters is principally through anaerobic, bacterial decay of organic substances in bottom sediments and stratified lakes and reservoirs. Traces of sulphide ion occur in unpolluted bottom sediments from the decay of vegetation, but the presence of high concentrations often indicates the occurrence of sewage or industrial wastes. Under aerobic conditions, the sulphide ion converts rapidly to sulphur and sulphate ions.

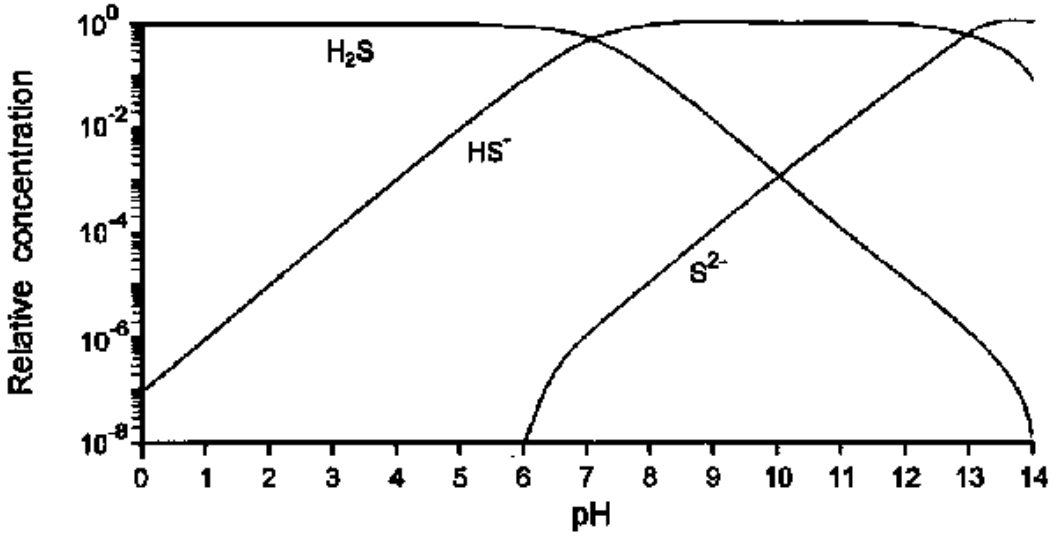
Dissolved sulphides exist in water as non-ionised molecules of hydrogen sulphide (H_2S), hydrosulphide (HS^-) and, very rarely, as sulphide (S^{2-}). The equilibrium between these forms is a function of pH (Figure 3.4). Sulphide concentrations need not be considered if the pH is lower than 10. Suspended matter may also contain various metallic sulphides. When appreciable concentrations of sulphide occur, toxicity and the strong odour of the sulphide ion make the water unsuitable for drinking water supplies and other uses.

Sulphide determination should be done immediately after sampling. If this is not possible, the sample should be fixed with cadmium acetate or zinc acetate, after which it can be stored for up to three days in the dark. During sampling, aeration of the sample must be prevented. Total sulphide, dissolved sulphide and free H_2S are the most significant determinations. Variations of pre-treatment (filtration and pH reduction) are used for their speciation. Photometric methods or, at high concentrations, iodometric titration are generally used for sulphide determination.

3.7.2. Silica

Silica is widespread and always present in surface and groundwaters. It exists in water in dissolved, suspended and colloidal states. Dissolved forms are represented mostly by silicic acid, products of its dissociation and association, and organosilicon compounds. Reactive silicon (principally silicic acid but usually recorded as dissolved silica (SiO_2) or sometimes as silicate (H_4SiO_4)) mainly arises from chemical weathering of siliceous minerals. Silica may be discharged into water bodies with wastewaters from industries using siliceous compounds in their processes such as potteries, glass works and abrasive manufacture. Silica is also an essential element for certain aquatic plants (principally diatoms). It is taken up during cell growth and released during decomposition and decay giving rise to seasonal fluctuations in concentrations, particularly in lakes.

Figure 3.4. Relative concentrations of the different forms of sulphide in relation to the pH of pure freshwaters



The silica content of rivers and lakes usually varies within the range 1-30 mg l^{-1}. Concentrations in ground and volcanic waters are higher, and thermal waters may reach concentrations up to 1 g l^{-1} or more. In the weakly mineralised waters of arctic regions, as well as in marsh and other coloured waters, the reactive silica may account for 50 per cent of the total dissolved solids.

Analytical determinations can be made for dissolved silicic acid (monomeric and dimeric forms), total dissolved silica including polymeric and organic species and suspended or total silica. Plastic containers must be used for samples intended for silica analysis. The samples can be stored without preservation for up to one week, provided they are kept at a low temperature and in the dark. Forms of silicon and total silica are converted to the reactive form prior to analysis using a colourimetric method. Atomic absorption spectrophotometry can also be used.

3.7.3. Fluoride

Fluoride originates from the weathering of fluoride-containing minerals and enters surface waters with run-off and groundwaters through direct contact. Liquid and gas emissions from certain industrial processes (such as metal-and chemical-based manufacturing) can also contribute fluoride ions (F^-) to water bodies. Fluoride mobility in water depends, to a large extent, on the Ca^{2+} ion content, since fluoride forms low solubility compounds with divalent cations. Other ions that determine water hardness can also increase F^- solubility.

Fluoride concentrations in natural waters vary from 0.05 to 100 mg l^{-1}, although in most situations they are less than 0.1 mg l^{-1}. Groundwater concentrations are often as high as 10 mg l^{-1}. Very high concentrations of fluoride, far exceeding the WHO guideline value of 1.5 mg l^{-1} (Table 3.4), are encountered in volcanic aquifers and lakes in the East African Rift system and in Hawaii. Localised occurrences of high fluoride in groundwater associated with sedimentary and metamorphic rocks are also reported from Ohio, Sri Lanka, India, Malawi and Tanzania. Fluctuations from year to year are rarely more than two times the base level, or less, for groundwaters.

Measurement of fluoride content is especially important when a water body is used for drinking water supply. At high concentrations fluoride is toxic to humans and animals and can cause bone diseases. However, a slight increase in natural concentrations can help prevent dental caries although, at higher concentrations (above 1.5-2.0 mg l^{-1}), mottling of teeth can occur (WHO, 1984). High fluoride concentrations provide a constraint on the use of groundwaters for potable supply, which may present particular difficulties where there is no practical alternative to groundwater and such values are unlikely to change with time. Where fluoride is known to occur or can be anticipated, it is an essential variable in surveys where community water supplies are being planned but for long-term monitoring it is less important.

Water samples for fluoride determination do not usually require any preservation and can be analysed up to several days following collection. Storage in polyethylene containers is recommended. Determination of the fluoride ion can be made potentiometrically (with a fluoride ion selective electrode) or photometrically. Interference effects from metals in the water can be eliminated by distillation or ion-exchange chromatography.

3.7.4. Boron

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

Despite its widespread occurrence, boron is usually present in natural waters in comparatively low concentrations. Average concentrations in surface waters do not exceed 0.1 mg l^{-1} and only reach 1.5-3 mg l^{-1} in a few areas. Higher concentrations of boron (up to 48 mg l^{-1}) are found in some mineral waters which are sometimes used for

special health-related bathing, but not as drinking water. Maximum allowable concentrations of boron in water bodies used for drinking water vary in different countries (Table 3.4). Recommended concentrations of boron in waters used for irrigation vary from 0.5 mg l^{-1} for sensitive crops to 6 mg l^{-1} for short-term irrigation or for tolerant crops.

Containers for samples intended for boron determination must be made of polyethylene or alkali-resistant, boron-free glass. Analysis is normally by photometric methods.

3.7.5. Cyanide

Compounds of cyanide enter freshwaters with wastewaters from industries such as the electroplating industry. Cyanides occur in waters in ionic form or as weakly dissociated hydrocyanic acid. In addition, they may occur as complex compounds with metals. The toxicity of cyanides depends on their speciation; some ionic forms and hydrocyanic acid are highly toxic. The toxicity of complex compounds of cyanide depends on their stability. Weak complexes formed with metals such as zinc, lead and cadmium are extremely toxic. Copper complexes are less toxic, and cobalt and ferrous complexes are only weak toxicants.

Ionic cyanide concentration in water is reduced by carbonic and other acids transforming the ionic form into the volatile hydrocyanic acid. However, the principal mechanism of decreased levels is oxidation, including biochemical oxidation, followed by hydrolysis:

$$2CN^- + O_2 = 2CNO^-; \; CNO^- + 2H_2O = NH_4^+ + CO_3^{2-}.$$

Strong sunlight and warm seasons favour biochemical oxidation causing a reduction in cyanide concentrations. Cyanides, especially ionic forms, are easily adsorbed by suspended matter and bottom sediments.

Concentrations of cyanides in waters intended for human use, including complex forms (except hexacyanoferrate), are strictly limited because of their high toxicity. The WHO recommends a maximum concentration of 0.07 mg l^{-1} cyanide in drinking water, but many countries apply stricter standards of cyanide concentration both for drinking waters and natural water of importance for fisheries (Table 3.4).

Samples for cyanide determination must be analysed as soon as possible because it is a highly active and unstable variable. If necessary, samples collected in polyethylene bottles can be preserved with sufficient sodium hydroxide to raise the pH to 11 or more and then stored at about 4° C. A photometric method is normally used for the determination of cyanides in natural waters. A preliminary distillation of cyanides as hydrocyanic acid after acidification, should be made if there are any compounds causing interference in the water, or if the cyanide concentration is too low for direct determination. However, distillation should only be used when really necessary, because the product is very toxic, requiring special safety procedures.

3.8. Metals

3.8.1. General principles

The ability of a water body to support aquatic life, as well as its suitability for other uses, depends on many trace elements. Some metals, such as Mn, Zn and Cu, when present in trace concentrations are important for the physiological functions of living tissue and regulate many biochemical processes. The same metals, however, discharged into natural waters at increased concentrations in sewage, industrial effluents or from mining operations can have severe toxicological effects on humans and the aquatic ecosystem. Water pollution by heavy metals as a result of human activities is causing serious ecological problems in many parts of the world. This situation is aggravated by the lack of natural elimination processes for metals. As a result, metals shift from one compartment within the aquatic environment to another, including the biota, often with detrimental effects. Where sufficient accumulation of the metals in biota occurs through food chain transfer (see Chapter 5), there is also an increasing toxicological risk for humans. As a result of adsorption and accumulation, the concentration of metals in bottom sediments is much higher than in the water above and this sometimes causes secondary pollution problems.

Generally, trace amounts of metals are always present in freshwaters from the weathering of rocks and soils. In addition, particularly in developed countries, industrial wastewater discharges and mining are major sources of metals in freshwaters. Significant amounts also enter surface waters in sewage as well as with atmospheric deposition (e.g. lead). Lead is still widely used as an additive in petroleum for automobiles and is emitted to the atmosphere in their exhaust gases, thereby entering the hydrological cycle.

The toxicity of metals in water depends on the degree of oxidation of a given metal ion together with the forms in which it occurs. For example, the maximum allowable concentration of Cr (VI) in the former USSR was 0.001 mg l^{-1} whereas for Cr (III) it was 0.5 mg l^{-1} (Bestemyanov and Krotov, 1985). As a rule, the ionic form of a metal is the most toxic form. However, the toxicity is reduced if the ions are bound into complexes with, for example, natural organic matter such as fulvic and humic acids. Under certain conditions, metallo-organic, low-molecular compounds formed in natural waters exhibit toxicities greater than the uncombined forms. An example is the highly toxic alkyl-derivatives of mercury (e.g. methylmercury) formed from elemental mercury by aquatic micro-organisms.

Metals in natural waters can exist in truly dissolved, colloidal and suspended forms. The proportion of these forms varies for different metals and for different water bodies. Consequently, the toxicity and sedimentation potential of metals change, depending on their forms.

The assessment of metal pollution is an important aspect of most water quality assessment programmes. The Global Environment Monitoring System (GEMS) programme GEMS/WATER includes ten metals: Al, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn. Arsenic and Se (which are not strictly metals) are also included (Table 3.5). The United States Environmental Protection Agency (US EPA) considers eight trace elements as high priority: As, Cd, Cu, Cr, Pb, Hg, Ni and Zn. Most other countries include the same

metals in their priority lists. However, other highly toxic metals such as Be, Tl, V, Sb, Mo should also be monitored where they are likely to occur.

The absence of iron and manganese in some priority lists results from their frequent classification as major elements. The occurrence of iron in aqueous solution is dependent on environmental conditions, especially oxidation and reduction. Flowing surface water, that is fully aerated, should not contain more than a few micrograms per litre of uncomplexed dissolved iron at equilibrium in the pH range 6.6 to 8.5. In groundwater, however, much higher levels can occur. In anoxic groundwaters with a pH of 6 to 8, ferrous iron (Fe^{2+}) concentrations can be as high as 50 mg l^{-1} and concentrations of 1 to 10 mg l^{-1} are common. The iron originates by solution at sites of either reduction of ferric hydroxides or oxidation of ferrous sulphide (Hem, 1989) and the process is strongly influenced by microbiological activity. Reduced groundwater is clear when first brought from a well but becomes cloudy, and then orange in colour, as oxidation immediately occurs with the precipitation of ferric hydroxide. Consequently, obtaining representative samples for iron determination from groundwaters presents special difficulties. High iron concentrations in groundwater are widely reported from developing countries, where iron is often an important water quality issue. Similar problems can be found in anoxic waters for Mn^{2+}, although the concentrations reached are usually ten times less than ferrous iron.

The concentration of different metals in waters varies over a wide range (0.1-0.001 µg l^{-1}) at background sites and can rise to concentrations which are dangerous for human health in some water bodies influenced by human activities. Dissolved metal concentrations are particularly difficult to measure due to possible contamination during sampling, pre-treatment and storage. As a result, large differences may be observed between analyses performed by highly specialised teams. The natural variability of dissolved metals is not yet fully understood. As dissolved metals occur in very low concentrations, it is recommended that metals are measured in the particulate matter, for which there is much more information on variability, reference background values, etc. (see Tables 4.1 and 4.2).

Table 3.5. Variables included in the GEMS/WATER monitoring programme at baseline and global flux stations[1]

Variable	Baseline stations		Global river flux stations
	Streams	Headwater lakes	
Basic monitoring			
Water discharge/level	x		x[2]
Total suspended solids	x		x
Transparency		x	
Temperature	x	x	x
pH	x	x	x
Conductivity	x	x	x
Dissolved oxygen	x	x	x
Calcium	x	x	x

Magnesium	x	x	x
Sodium	x	x	x
Potassium	x	x	x
Chloride	x	x	x
Sulphate	x	x	x
Alkalinity	x	x	x
Nitrate plus nitrite	x	x	x
Ammonia	x		x
Total phosphorus, unfiltered	x	x	x
Total phosphorus, dissolved	x	x	x
Reactive silica	x	x	x
Chlorophyll *a*	x	x	x
Expanded monitoring			
Total phosphorus, unfiltered			x
Dissolved organic carbon	x	x	x
Particulate organic carbon			x
Dissolved organic nitrogen	x	x	x
Particulate organic nitrogen			x
Aluminium	x[3]	x[3]	x[4]
Iron	x[3]	x[3]	x[4]
Manganese	x[3]	x[3]	x[4]
Arsenic[5]	x[3]	x[3]	x[4]
Cadmium[5]	x[3]	x[3]	x[4]
Chromium			x[4]
Copper			x[4]
Lead[5]	x[6]	x[6]	x[4]
Mercury[5]	x[6]	x[6]	x[4]
Selenium			x[4]
Zinc[5]	x[3]	x[3]	x[4]
Total hydrocarbons			x[7]
Total polyaromatic hydrocarbons			x[7]
Total chlorinated hydrocarbons			x[7]
Dieldrin			x[7]
Aldrin			x[7]
Sum of DDTs[5]	x	x	x[7]
Atrazine	x	x	x[7]
Sum of PCBs[5]			x[7]
Phenols			x[7]

[1] The selection of variables for trend monitoring is related to different pollution issues

[2] Continuous monitoring

[3] Dissolved only
[4] Dissolved and particulate
[5] Included as contaminant monitoring at baseline stations
[6] Total
[7] Unfiltered water samples

Source: WHO, 1991

The variety of metal species is the main methodological difficulty in designing metal-based monitoring programmes. When checking compliance with water quality guidelines, for example, metals should always be determined in the same forms as those for which the guidelines or standards are set. If the quality standards refer to the dissolved forms of metals, only dissolved forms should be monitored. More than 50 per cent of the total metal present (and up to 99.9 per cent) is usually adsorbed onto suspended particles; this is particularly relevant when assessing metal discharge by rivers (see Chapter 4). Consequently, monitoring and assessment programmes such as GEMS/WATER include the determination of both total (unfiltered) and dissolved (filtered through 0.45 µm filter) concentrations of metals when assessing the flux of contaminants into the oceans. More detailed investigations involving the speciation and partition of the metals are rather complicated and should be carried out in special situations only (Hem, 1989).

3.8.2. Sampling and measurement

Samples for metal analysis are usually pre-treated by acidification prior to transportation to the laboratory to suppress hydrolysis, sorption and other processes which affect concentration. However, such preservation techniques destroy the equilibrium of the different forms of the metals, and can be used only for determination of total concentrations. For determination of dissolved metals, it is recommended that the samples are filtered through 0.45 µm pore diameter membrane filters (using ultra-clean equipment in a laminar flow hood). The filtered sample should be acidified for preservation. Removal of the particulate matter by filtration prevents dissolution or desorption of trace metals from the particulate phase to the dissolved phase within the sample. A very high degree of cleanliness in sample handling at all stages of collection and analysis is necessary (such as, use of ultra-pure acids to clean glassware or PTFE (polytetrafluoroethene) utensils, use of a laminar flow hood for sample manipulation and special laboratories with air filtration and purification systems) to avoid contamination and incorrect results.

The low concentrations of metals in natural waters necessitate determination by instrumental methods. Photometric methods, sometimes in combination with extraction, are the oldest and most inexpensive techniques (see various methods handbooks). However, as these have high detection limits, they can only be used for analysis of comparatively polluted waters. Atomic absorption methods are the most widely used. Atomic absorption with flame atomisation is the most simple and available modification of this method, but application for direct determination of metals is possible only if concentrations exceed 50 µg l^{-1}. In other cases, it is necessary to use preconcentration. Atomic absorption with electrothermal atomisation allows direct determination of metals at virtually the full range of concentrations typically found in freshwaters. However, this is a more expensive method requiring specially trained personnel. Even with this method special measures may be needed to eliminate matrix effects.

Atomic emission spectroscopy methods are able to determine a large number of elements simultaneously. Inductively coupled plasma atomic emission spectrometry is becoming popular, especially in the industrially developed countries, due to its high productivity and wide range of quantifiable determinations (despite the high cost of the equipment and the large argon consumption necessary for creating the plasma atmosphere). In contrast, spectrographical analysis is becoming less popular because it is time and labour intensive and has low accuracy.

3.9. Organic contaminants

3.9.1. General principles

Many thousands of individual organic compounds enter water bodies as a result of human activities. These compounds have significantly different physical, chemical and toxicological properties. Monitoring every individual compound is not feasible. However, it is possible to select priority organic pollutants based on their prevalence, toxicity and other properties. Mineral oil, petroleum products, phenols, pesticides, polychlorinated biphenyls (PCBs) and surfactants are examples of such classes of compounds. However, these compounds are not monitored in all circumstances, because their determination requires sophisticated instrumentation and highly trained personnel. In the future much effort will be needed in monitoring these classes of compounds because they are becoming widespread and have adverse effects on humans and the aquatic environment.

When selecting a list of variables for a survey of organic contaminants, the gross parameters of TOC, COD and BOD should be included. In addition, during preliminary surveys and in emergencies, the whole range of individual organic compounds should be identified. This requires sophisticated instrumental methods, including gas chromatography (GC), liquid chromatography (LC) and gas chromatography/mass spectrometry (GC/MS), in combination with effective pre-concentration. In intensive surveys, the following classes of organic pollutants should be identified: hydrocarbons (including aromatic and polyaromatic), purgeable halocarbons, chlorinated hydrocarbons, different pesticide groups, PCBs, phenols, phthalate esters, nitrosamines, nitroaromatics, haloethers, benzidine derivatives and dioxins. In most cases, analysis for organic contaminants is performed on unfiltered water samples. However, variations observed in samples from turbid rivers may largely reflect variations in total suspended solids. Consequently, it is recommended that analysis of the less soluble organic contaminants (e.g. organochlorine pesticides) is carried out on the particulate material (collected by filtration or centrifugation) in the samples (see Chapter 4).

3.9.2. Mineral oil and petroleum products

Mineral oil and petroleum products are major pollutants responsible for ecological damage especially in inland surface waters. At present, more than 800 individual compounds have been identified in mineral oils. Among them are low- and high-molecular weight aliphatic, aromatic and naphthenic hydrocarbons (or petroleum products), high-molecular unsaturated heterocyclic compounds (resins and asphaltenes) as well as numerous oxygen, nitrogen and sulphur compounds (Table 3.6).

Oil is distributed in water bodies in different forms: dissolved, film, emulsion and sorbed fractions. Interactions between these fractions are complicated and diverse, and depend on the specific gravities, boiling points, surface tensions, viscosities, solubilities and sorption capabilities of the compounds present. In addition, transformation of oil compounds by biochemical, microbiological, chemical and photochemical processes occurs simultaneously. Due to the high ecological risk associated with oil extraction, transportation, refining and use, mineral oil is considered a priority pollutant and its determination is important for assessments related to these activities.

Table 3.6. The main components of mineral oils

Component group	Content (%)
Hydrocarbons:	
paraffinic	10-70
naphthenic (mono- and polycyclic)	25-75
aromatic (mono- and polycyclic)	6-40
naphthenon-aromatic	30-70
Unsaturated heterocyclic compounds:	
resins	1-40
asphaltenes	0-80
asphaltenic acids and their anhydrites	0-7

The permissible concentration of mineral oil and petroleum products in water depends on the intended use of the water. The recommended maximum concentrations for drinking water supplies and fisheries protection are generally between 0.01 and 0.1 mg l^{-1}. Concentrations of 0.3 mg l^{-1} or more of crude oil can cause toxic effects in freshwater fish.

Since hydrocarbons are the principal component fraction of oils, the definition “petroleum products” applies only to this fraction to ensure comparability of analytical data. The total concentration of dissolved and emulsified oils is the more usual determination and dissolved, emulsified and other fractions should only be determined separately in special cases.

As oil can be biochemically oxidised very easily, it is necessary to extract it from the sample immediately after sampling with carbon tetrachloride or trichlorotrifluoroethane. The extract can then be stored in a cool, dark place for several months. Gravimetric methods of oil determination are the most simple, but are not very sensitive and can give erroneous results due to the loss of volatile components. Ultra violet (UV), infra red (IR) spectrophotometric and luminescent methods are the most popular. Analysis based on column and thin-layer chromatographic separation allows the possibility of the separate determination of volatile and non-volatile polyaromatic hydrocarbons, resins and asphaltenes. Identification and determination of individual oil components is a complicated analytical task which can be undertaken only with the application of capillary gas chromatography, with either mass-spectrometric detection or luminescent spectrometry.

3.9.3. Phenols

Phenols are an important group of pollutants which enter water bodies in the waste discharges of many different industries. They are also formed naturally during the metabolism of aquatic organisms, biochemical decay and transformation of organic matter, in the water column and in bottom sediments.

Phenols are aromatic compounds with one or few hydroxy groups. They are easily biochemically, photochemically or chemically oxidised. As a result, they have detrimental effects on the quality and ecological condition of water bodies through direct effects on living organisms and the significant alteration of biogeneous elements and dissolved gases, principally oxygen.

The presence of phenols causes a marked deterioration in the organoleptic characteristics of water and as a result they are strictly controlled in drinking water and drinking water supplies. Concentrations of phenols in unpolluted waters are usually less than 0.02 mg l^{-1}. However, toxic effects on fish can be observed at concentrations of 0.01 mg l^{-1} and above.

Phenols are usually divided into two groups: steam-distillable phenols (phenol, cresols, xylenes, chlorphenols, etc.) and non-distillable phenols (catechol, hydroquinone, naphthols, etc.). The analytical method used with steam distillation determines only the volatile phenol fractions; these have the worst effects on organoleptic water characteristics. The method does not detect non-volatile phenols which, unfortunately, are often present in greater quantities than the volatile phenols and, furthermore, tend to be highly toxic. Chromatographic determination of individual phenols is more informative, but requires sophisticated instrumentation.

Samples, particularly if required for the determination of volatile phenols, must not be stored for long periods and, ideally, determination should be carried out within four hours. If this is not possible, samples can be preserved with sodium hydroxide and stored for 3-4 days at 2-4° C.

3.9.4 Pesticides

Pesticides are chemical compounds toxic to certain living organisms, from bacteria and fungi up to higher plants and even mammals. Most pesticides are compounds which do not occur naturally in the environment and, therefore, detectable concentrations indicate pollution. There are approximately 10,000 different pesticides currently available. The most widely used are insecticides (for extermination of insects), herbicides (for extermination of weeds and other undesirable plants) and fungicides (for preventing fungal diseases).

The mode of action of a pesticide is determined by its chemical structure. These structures are similar for the related compounds which comprise separate classes of pesticides such as the organochlorine pesticides, organophosphorus pesticides, the carbamate pesticides, the triazine herbicides and chlorphenolic acids.

The monitoring of pesticides presents considerable difficulties, particularly for groundwaters. There is a wide range of pesticides in common agricultural use, and many

of them break down into toxic products. Screening of water samples for all compounds is very expensive; therefore, a preliminary survey of local pesticide use needs to be carried out to reduce the number of target compounds in each specific assessment programme.

Internationally there is considerable variation between, and uncertainty over, guidelines on permissible concentrations of pesticides in drinking water. Nevertheless, the guideline values are at the microgram per litre level which, for the most toxic compounds, are close to the limits of analytical detection. Highly sophisticated analytical procedures are necessary, which normally require a combination of a directly-coupled gas chromatograph (GC) and mass spectrometer (MS). Some pesticides are very polar and cannot be extracted from water for injection into a GC. Furthermore, some other pesticides are too chemically unstable to be heated in a GC. High pressure liquid chromatography is showing promise as a means of isolating compounds in both of these categories. A high degree of cleanliness is necessary for sample handling at all stages, such as the use of ultra-clean solvents to clean glass or stainless steel apparatus.

Organochlorine pesticides

Environmental levels of organochlorine pesticides tend to be higher than other pesticides because of their widespread and prolonged use, combined with their great chemical stability. In the 1950s, DDT was used liberally around the world, but at the beginning of the 1970s most countries severely limited, or even prohibited, its use. However, concentrations of DDT and its metabolites (DDD, DDE) are still high in many environments, especially in arid areas.

Organochlorine pesticides are chlorine derivatives of polynuclear hydrocarbons (e.g. DDT), cycloparaffins (e.g. hexachlorocyclohexane (HCH)), compounds of the diene series (e.g. heptachlor) and aliphatic carbonic acids (e.g. propanide). Most of the compounds are hydrophobic (insoluble in water) but highly soluble in hydrocarbons and fats. They have the ability to accumulate in biological tissues, reaching much higher concentrations in certain aquatic biota than in the surrounding water and sediments (see Chapter 5). The affinity of pesticides for adsorption onto mineral suspended matter and organic colloids is important for their distribution and mobility in water bodies. Bottom sediments also play a significant role in storage and transformation of organochlorine pesticides.

Where present, concentrations of organochlorine pesticides in water bodies tend to be in the range 10^{-5}-10^{-3} mg l^{-1}. These compounds and their metabolites have been found in sites as distant as the Arctic and Antarctic regions as a result of long-range atmospheric transport. They are sometimes found in groundwaters, where leaching from disposal sites for hazardous substances or from agricultural land usually accounts for their presence. As these compounds are hydrophobic, their occurrence in groundwater may be the result of “solubilisation” in fulvic acid materials.

Due to their toxicity, the maximum allowable concentrations of organochlorine pesticides must be strictly adhered to in waters important for their fish communities or used for drinking water supplies.

Organophosphorus pesticides

Organophosphorus pesticides are complex esters of phosphoric, thiophosphoric and other phosphorus acids. They are widely applied as insecticides, acaricides and defoliants. Their relatively low chemical and biochemical stability is an advantage because many decompose in the environment within a month. Organophosphorus pesticides, like organochlorine pesticides, are readily adsorbed onto suspended matter. Photolysis, as well as hydrolitic, oxidation and enzyme decay processes are the principal mechanisms of decay, resulting in detoxification. When found, the concentrations of Organophosphorus pesticides in surface waters range from 10^{-3}-10^{-2} mg l^{-1}.

Unfiltered samples for organochlorine and organophosphorus determination should be collected in glass containers with PTFE caps. Samples can be stored for a short time at low temperature. However, immediate extraction followed by storage at -15° C is preferable. In this case, samples may be stored for up to three weeks.

3.9.5. Surfactants

Synthetic surfactants are compounds belonging to different chemical classes but containing a weak-polar hydrophobic radical (e.g. alkyl or alkylaryl) and one or more polar groups. They can be classified into anionic (negatively charged), cationic (positively charged) and nonionic (non-ionising). Anionic surfactants are the most widely produced and used, usually as detergents.

Surfactants enter water bodies with industrial and household wastewaters. Atmospheric inputs (originating from atmospheric discharges from surfactant-producing plants) in the form of precipitation are also significant. Surfactants can exist in surface waters in the dissolved or adsorbed states, as well as in the surface film of water bodies, because they have a pronounced ability to concentrate at the air-water or water-sediment interface. Although surfactants are not highly toxic, they can affect aquatic biota. Detergents can impart taste or odour to water at concentrations of 0.4-3 mg l^{-1} and chlorination can increase this effect. Surfactants are responsible for foam formation in surface waters and other pollutants, including pathogens, can become concentrated in the foam. The presence of foam on the water surface makes water aeration difficult, lowering oxygen levels, reducing self-purification processes and adversely affecting aquatic biota. The threshold concentration for foam formation is 0.1-0.5 mg l^{-1} depending on the structure of the surfactant.

In terms of biodegradability, surfactants are divided into highly degradable, intermediate and stable, or non-degradable, with corresponding biochemical oxidation rate constants of > 0.30 day^{-1}, 0.30-0.05 day^{-1} and < 0.05 day^{-1} respectively. In recent years there has been a tendency to substitute non-degradable surfactants for degradable ones. However, this approach to reducing pollution has the drawback of causing a significant decrease in dissolved oxygen concentrations.

The inherent properties of surfactants require special procedures for sample preservation, principally to avoid foam formation and their adsorption onto the walls of the sample containers. Photometric methods are the most widely used for determination of all three types of surfactants and are well documented. Analytical methods are sufficiently simple and convenient for application in any laboratory.

3.10. Microbiological indicators

The most common risk to human health associated with water stems from the presence of disease-causing micro-organisms. Many of these microorganisms originate from water polluted with human excrement. Human faeces can contain a variety of intestinal pathogens which cause diseases ranging from mild gastro-enteritis to the serious, and possibly fatal, dysentery, cholera and typhoid. Depending on the prevalence of certain other diseases in a community, other viruses and parasites may also be present. Freshwaters also contain indigenous micro-organisms, including bacteria, fungi, protozoa (single-celled organisms) and algae (micro-organisms with photosynthetic pigments), a few of which are known to produce toxins and transmit, or cause, diseases.

Intestinal bacterial pathogens are distributed world-wide, the most common water-borne bacterial pathogens being *Salmonella, Shigella,* enterotoxigenic *Escherichia coli, Campylobacter, Vibrio* and *Yersinia.* Other pathogens occasionally found include *Mycobacterium, Pasteurella, Leptospira* and *Legionella* and the enteroviruses (poliovirus, echo virus and Coxsackie virus). Adenoviruses, reoviruses, rotaviruses and the hepatitis virus may also occur in water bodies. All viruses are highly infectious. *Salmonella* species, responsible for typhoid, paratyphoid, gastro-enteritis and food poisoning, can be excreted by an apparently healthy person acting as a carrier and they can also be carried by some birds and animals. Therefore, contamination of water bodies by animal or human excrement introduces the risk of infection to those who use the water for drinking, food preparation, personal hygiene and even recreation.

Sewage, agricultural and urban run-off, and domestic wastewaters are widely discharged to water bodies, particularly rivers. Pathogens associated with these discharges subsequently become distributed through the water body presenting a risk to downstream water users. Typical municipal raw sewage can contain 10 to 100 million coliform bacteria (bacteria originating from the gut) per 100 ml, and 1 to 50 million *Escherichia coli* or faecal streptococci per 100 ml. Different levels of wastewater treatment may reduce this by a factor of 10 to 100 and concentrations are reduced further after dilution by the receiving waters.

The practice of land application of wastewaters, particularly poorly treated wastewaters, can lead to pathogen contamination of surface and ground-waters. Surface water contamination is usually as a result of careless spraying or run-off, and groundwater pollution arises from rapid percolation through soils. Other sources of pathogens are run-off and leachates from sanitary landfills and urban solid waste disposal sites which contain domestic animal and human faecal material. The use of water bodies by domestic livestock and wildlife is also a potential source of pathogens.

The survival of microbiological pathogens, once discharged into a water body, is highly variable depending on the quality of the receiving waters, particularly the turbidity, oxygen levels, nutrients and temperature. *Salmonella* bacilli have been reported in excess of 50 miles downstream of the point source, indicating an ability to survive, under the right conditions, for several days. Once in a water body, micro-organisms often become adsorbed onto sand, clay and sediment particles. The settling of these particles results in the accumulation of the organisms in river and lake sediments. The speed at which the settling occurs depends on the velocity and turbulence of the water body.

Some removal of micro-organisms from the water column also occurs as a result of predation by filter feeding microzooplankton.

Counts of bacteria of faecal origin in rivers and lakes around the world which suffer little human impact vary from < 1 to 3,000 organisms per 100 ml. However, water bodies in areas of high population density can have counts up to 10 million organisms per 100 ml. Natural groundwaters should contain no faecal bacteria unless contaminated, whereas surface waters, even in remote mountain areas, may contain up to 100 per 100 ml. To avoid human infection, the WHO recommended concentration for drinking water is zero organisms per 100 ml. Detection of pathogens other than faecal bacteria, particularly viruses, is less common partly due to the lack of appropriate, routinely available methodology. *Salmonella* organisms have been recorded at concentrations 10 to 20 times less than the faecal coliform numbers in the same sample. Where faecal coliform bacteria counts are high, viruses may also be detectable, but only in volumes of 20 to 100 litres of water. Enteroviruses occur in raw sewage at very much lower concentrations than bacterial pathogens; measured as plaque forming units (PFUs) they rarely occur at more than 1,000 units per litre.

Monitoring for the presence of pathogenic bacteria is an essential component of any water quality assessment where water use, directly or indirectly, leads to human ingestion. Such uses include drinking, personal hygiene, recreation (e.g. swimming, boating), irrigation of food crops and food washing and processing. Monitoring to detect pathogens can be carried out without accompanying physical and chemical measurements and, therefore, can be very inexpensive.

Prior to using any new drinking water source it should be examined for the presence of faecal bacteria. Sampling localities should be carefully chosen so that the source of the contamination can be identified and removed. Even when drinking water sources have been subjected to treatment and disinfection, it is essential that routine examination of the supply is carried out at weekly, or even daily intervals where the population at risk is large (tens or hundreds of thousands). Where water is used mainly for personal hygiene or recreation, there is still a risk of accidental ingestion of intestinal pathogens as well as a risk of other infections, particularly in the eyes, ears and nose. Less than 10^3 coliforms per 100 ml presents little risk of intestinal diseases although the risk of virus-borne infections always remains.

Where irrigation with wastewater is carried out by spraying food crops, it is advisable to monitor for faecal bacteria as there is a risk of contamination to those eating the crop. This risk is less when irrigation is ceased some time before harvest, as many bacteria do not survive for long periods unless in ideal conditions of temperature and nutrients. The use of contaminated water in any stage of food processing presents a serious risk to human health as food provides an ideal growth medium. All water which may come into contact with food must, therefore, be checked for faecal contamination. Where treated water is temporarily stored in a tank it should be examined immediately prior to use.

Faecal contamination can be measured to indicate the presence of organic pollution of human origin. Other naturally present micro-organisms, such as the algal and protozoan communities may, however, in some situations be more useful to gain an insight into the level of pollution (see Chapter 5).

Methods for detection of the presence of faecal material have been developed which are based on the presence of “indicator” organisms, such as the normal intestinal bacterium *Escherichia coli* (see Chapter 5 for further details). Such methods are cheap and simple to perform and some have been developed into field kits, particularly for use in developing countries (Bartram and Ballance, 1996). Positive identification of the pathogenic bacteria *Salmonella, Shigella* or *Vibrio* spp. can be quite complex, requiring several different methods. A special survey may be undertaken if a source of an epidemic is suspected, or if a new drinking water supply is being tested. As these organisms usually occur in very low numbers in water samples, it is necessary to concentrate the samples by a filtration technique prior to the analysis. Although methodologies for identification of viruses are constantly being improved and simplified, they require advanced and expensive laboratory facilities. Local or regional authorities responsible for water quality may be unable to provide such facilities. However, suitably collected and prepared samples can easily be transported, making it feasible to have one national or regional laboratory capable of such analyses. Sample collection kits have been developed for use in such situations.

3.11. Selection of variables

The selection of variables to be included in a water quality assessment must be related to the objectives of the programme (see Chapters 1 and 2). The various types of monitoring operations and their principal uses have been given in Table 2.1. Broadly, assessments can be divided into two categories, use-orientated and impact-orientated. In addition, operational surveillance can be used to check the efficiency of water treatment processes by monitoring the quality of effluents or treated waters, but this is not discussed here.

3.11.1. Selection of variables in relation to water use

Use-orientated assessment tests whether water quality is satisfactory for specific purposes, such as drinking water supply, industrial use or irrigation. Many water uses have specific requirements with respect to physical and chemical variables or contaminants. In some cases, therefore, the required quality of the water has been defined by guidelines, standards or maximum allowable concentrations (see Table 3.4). These consist of recommended (as in the case of guidelines) or mandatory (as in the case of standards) concentrations of selected variables which should not be exceeded for the prescribed water use. For some variables, the defined concentrations vary from country to country (Table 3.4). Existing guidelines and standards define the minimum set of variables for inclusion in assessment programmes. Tables 3.7 and 3.8 suggest variables appropriate to specific water uses and can be used where guidelines are not available. Other variables can also be monitored, if necessary, according to special conditions related to the intended use. Acceptable water quality is also related to water availability. When water is scarce, a lower level of quality may have to be accepted and the variables measured can be kept to a minimum.

Background monitoring

The water quality of unpolluted water bodies is dependent on the local geological, biological and climatological conditions. These conditions control the mineral quality, ion balances and biological cycles of the water body. To preserve the quality of the aquatic

environment, the natural balances should be maintained. A knowledge of the background quality is necessary to assess the suitability of water for use and to detect future human impacts. Background quality also serves as a “control” for comparison with conditions at sites presently suffering from anthropogenic impacts. In most assessment programmes, some variables related to background water quality are always included, such as those suggested in Table 3.7.

Aquatic life and fisheries

Individual aquatic organisms have different requirements with respect to the physical and chemical characteristics of a water body. Available oxygen, adequate nutrients or food supply, and the absence of toxic chemicals are essential factors for growth and reproduction. Various guidelines have been proposed for waters important for fisheries or aquatic life (Table 3.4). Detailed information has been prepared by the European Inland Fisheries Advisory Commission (EIFAC) of the Food and Agriculture Organization of the United Nations (FAO) (EIFAC, 1964 onwards). As fish are an essential source of protein for man, it is imperative to avoid accumulation of contaminants in fish or shellfish (see Chapter 5). Suggested variables for inclusion in an assessment programme aimed at protecting aquatic life and fisheries are given in Table 3.7.

Table 3.7. Selection of variables for assessment of water quality in relation to non-industrial water use[1]

	Background monitoring	Aquatic life and fisheries	Drinking water sources	Recreation and health	Agriculture	
					Irrigation	Livestock watering
General variables						
Temperature	xxx	xxx		x		
Colour	xx		xx	xx		
Odour			xx	xx		
Suspended solids	xxx	xxx	xxx	xxx		
Turbidity/transparency	x	xx	xx	xx		
Conductivity	xx	x	x		x	
Total dissolved solids		x	x		xxx	x
pH	xxx	xx	x	x	xx	
Dissolved oxygen	xxx	xxx	x		x	
Hardness		x	xx			
Chlorophyll a	x	xx	xx	xx		
Nutrients						
Ammonia	x	xxx	x			
Nitrate/nitrite	xx	x	xxx			xx
Phosphorus or phosphate	xx					
Organic matter						
TOC	xx		x	x		

COD	xx	xx				
BOD	xxx	xxx	xx			
Major ions						
Sodium	x		x		xxx	
Potassium	x					
Calcium	x				x	x
Magnesium	xx		x			
Chloride	xx		x		xxx	
Sulphate	x		x			x
Other inorganic variables						
Fluoride			xx		x	x
Boron					xx	x
Cyanide		x	x			
Trace elements						
Heavy metals		xx	xxx		x	x
Arsenic & selenium		xx	xx		x	x
Organic contaminants						
Oil and hydrocarbons		x	xx	xx	x	x
Organic solvents		x	xxx[2]			x
Phenols		x	xx			x
Pesticides		xx	xx			x
Surfactants		x	x	x		x
Microbiological indicators						
Faecal coliforms			xxx	xxx	xxx	
Total coliforms			xxx	xxx	x	
Pathogens			xxx	xxx	x	xx

TOC Total organic carbon
BOD Biochemical oxygen demand
COD Chemical oxygen demand

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

The selection of variables should only include those most appropriate to local conditions and it may be necessary to include other variables not indicated under the above headings.

[1] For industrial uses see Table 3.8
[2] Extremely important in groundwater

Drinking water sources

In some regions groundwater, or water from rivers and lakes, is used for drinking without treatment. In other areas, it is subjected to treatment and/or disinfection before use. In both cases, the water which is eventually consumed should be monitored for variables which may pose a potential risk to human health. Guidelines for maximum concentrations of such variables in drinking water have been set by WHO (WHO, 1993) and regional and national authorities such as the Commission of the European Communities (CEC, 1980), US EPA (US EPA, 1993) and Environment Canada (Environment Canada, 1987) (Table 3.4). Drinking water sources should also be monitored to establish the required level of water treatment and to detect any contaminants which may not be removed during treatment, or which may interfere with the treatment process. Water ready for distribution and consumption can also be monitored to check the efficiency of the treatment process. Table 3.7 lists variables which should be measured with respect to recommended guidelines and those which are potentially a problem for drinking water sources. The selection of those which would actually be included in an assessment programme depends on the nature of the water source and the level of subsequent treatment. Many groundwater sources require minimal or no treatment and, consequently, need only be monitored infrequently for such variables as pathogens and organic solvents.

Recreation and health

Besides drinking, human populations use water for hygiene purposes (e.g. washing) and recreation (e.g. swimming and boating). Such activities have an associated health risk if the water is of poor quality due to the possibility of ingesting small quantities, or the pathogens directly entering the eyes, nose, ears or open wounds. Most recommended variables with respect to recreation and health are associated with pathogens or the aesthetic quality of the water (see Table 3.7). Guideline values are usually set with respect to use of the water for swimming (e.g. CEC, 1976) and other water-contact sports.

Agricultural use

Irrigation of food crops presents a possible health risk to food consumers if the quality of the irrigation water is inadequate, particularly with respect to pathogens and toxic compounds. The risk is greatest when the water is sprayed directly onto the crop rather than flooded around the base of the plants. The presence of certain inorganic ions can also affect the soil quality and, therefore, the growth potential of the crops. Recommended guidelines have been set for some variables in irrigation water (e.g. Environment Canada, 1987) but higher levels may be tolerated if water is scarce. Suggested variables for the monitoring of irrigation water are included in Table 3.7.

In principle, water for livestock watering should be of high quality to prevent livestock disease, salt imbalance or poisoning from toxic compounds. Nevertheless, higher levels of suspended solids and salinity may be tolerated by certain livestock than by humans.

Many of the variables included in monitoring the quality of livestock water are the same as for drinking water sources (see Table 3.7).

Industrial uses

The requirements of industry for water quality are diverse, depending on the nature of the industry and the individual processes using water within that industry. Table 3.8 summarises some of the key variables for some major industrial uses or processes. Although some guidelines have been proposed, they need to be considered in relation to the specific industrial needs and water availability.

Table 3.8. Selection of variables for the assessment of water quality in relation to some key industrial uses

	Heating	**Cooling**	**Power generation**	**Iron and steel**	**Pulp and paper**	**Petrol**	**Food processing**
General variables							
Temperature	xxx	xxx		xxx	x		
Colour	x				x		xx
Odour							xxx
Suspended solids	xxx	xxx	xx	xx	x	xxx	xx
Turbidity	xx				xx		xx
Conductivity	x	x					
Dissolved solids	xx	xx	xxx	xx	xxx	x	xxx
pH	x	xxx	xxx	xx	xx	xxx	xxx
Dissolved oxygen	xxx		x	xxx	x		
Hardness	xxx	xx	xxx	xx	xxx	xxx	xxx
Nutrients							
Ammonia	xxx		x				x
Nitrate						x	xx
Phosphate					x		
Organic matter							
COD		x	xx				
Major ions							
Calcium		xxx	xxx		x	xxx	x
Magnesium			x		x	xxx	x
Carbonate components	xx		xxx		xxx	x	x
Chloride	x	x	xx	xx	x	xxx	xxx
Sulphate		x	xx	xx	xx	x	xxx
Other inorganic variables							
Hydrogen sulphide	xxx	x					xx

Silica	xx	xx	x		x	x	x
Fluoride						x	xx
*Trace elements*x							
Aluminium		x	x				
Copper		x	x				
Iron	xx	x	x		x	x	xx
Manganese	xx	x	x		x		xx
Zinc			x				
Organic contaminants							
Oil & hydrocarbons	x	x	x	x			x
Organic solvents							x
Phenols							x
Pesticides							x
Surfactants	x	x	x				x
Microbiological indicators							
Pathogens							xxx

COD Chemical oxygen demand

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

3.11.2. Selection of variables in relation to pollutant sources

Water quality assessment often examines the effects of specific activities on water quality. Typically, such assessment is undertaken in relation to effluent discharges, urban or land run-off or accidental pollution incidents. The selection of variables is governed by knowledge of the pollution sources and the expected impacts on the receiving water body. It is also desirable to know the quality of the water prior to anthropogenic inputs. This can be obtained, for example, by monitoring upstream in a river or prior to the development of a proposed waste disposal facility. When this cannot be done, background water quality from an adjacent, uncontaminated, water body in the same catchment can be used. Appropriate variables for assessing water quality in relation to several major sources of pollutants are given in Tables 3.9 and 3.10.

Sewage and municipal wastewater

Municipal wastewaters consist of sewage effluents, urban drainage and other collected wastewaters. They usually contain high levels of faecal material and organic matter. Therefore, to assess the impact of such wastewaters it is advisable to measure variables which are indicative of organic waste such as BOD, COD, chloride, ammonia and nitrogen compounds. If the wastes contain sewage, then faecal indicators are also important. Depending on the collection and treatment systems in operation, municipal wastes may contain various other organic and inorganic contaminants of industrial origin.

Suggested variables for inclusion in an assessment programme are given in Table 3.9. Effluents from food processing also contain large amounts of organic matter and even pathogens, therefore, variables used to monitor the effects of food processing operations (Table 3.10) are similar to those for sewage and organic wastewater.

Table 3.9. Selection of variables for the assessment of water quality in relation to non-industrial pollution sources

	Sewage and municipal wastewater[1]	**Urban run-off**	**Agricultural activities**	**Waste disposal to land**		**Long range atmospheric transport**
				Solid municipal	**Hazardous chemicals**	
General variables						
Temperature	x	x	x			
Colour	x	x	x	x		
Odour	x	x	x			
Residues	x	x	xxx	xxx	xx	
Suspended solids	xxx	xx	xxx	xx	xx	
Conductivity	xx	xx	xx	xxx	xxx	xxx
Alkalinity				xx		xxx
pH	x	x	x	xx	xxx	xxx
Eh	x	x	x			
Dissolved oxygen	xxx	xxx	xxx	xxx	xxx	
Hardness	x	x	x		x	x
Nutrients						
Ammonia	xxx	xx	xxx	xx		
Nitrate/nitrite	xxx	xx	xxx	xx		xxx
Organic nitrogen	xxx	xx	xxx	xx		
Phosphorus compounds	xxx	xx	xxx	x		x
Organic matter						
TOC	x	x	x			
COD	xx	xx	x	xxx	xxx	
BOD	xxx	xx	xxx	xxx	xx	
Major ions						
Sodium	xx	xx	xx			
Potassium	x	x	x			
Calcium	x	x	x			
Magnesium	x	x	x			

Carbonate components						
Chloride	xxx	xx	xxx	xx	xx	
Sulphate	x	x	x			xxx
Other inorganic variables						
Sulphide	xx	xx	x		x	
Silica	x	x				
Fluoride	x	x				
Boron			x			
Trace elements						
Aluminium						xx
Cadmium		x		xxx	xxx	x
Chromium		x		xxx	xx	x
Copper	x	x	xx[2]	xxx	xx	x
Iron	xx	xx		xxx	xx	x
Lead	xx	xxx		xxx	xx	xx
Mercury	x	xx	xxx[2]	xxx	xxx	
Zinc			xx[2]	xxx	xx	x
Arsenic		x	xxx[2]	xx	xxx	x
Selenium		x	xxx[2]	x	x	
Organic contaminants						
Fats	x	x				
Oil and hydrocarbons	xx	xxx		xx	x	
Organic solvents	x	x		xxx	xxx	
Methane				xxx[3]		
Phenols	x			xx	xx	
Pesticides		x	xxx[4]	xx	xxx	xxx
Surfactants	xx		x		x	
Microbiological indicators						
Faecal coliforms	xxx	xx	xx	xxx		
Other pathogens	xxx		xx	xxx		

TOC Total organic carbon
COD Chemical oxygen demand
BOD Biochemical oxygen demand

x -xxx Low to high likelihood that the concentration of the variable will be affected and the more important it is to in-dude the variable in a monitoring programme.

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

[1] Assumes negligible industrial inputs to the wastewater
[2] Need only be measured when used locally or occur naturally at high concentrations
[3] Important only for groundwater in localised industrial areas
[4] Specific compounds should be measured according to their level of use in the region.

Urban run-off

Rivers running through, or lakes adjacent to, large urban developments are inevitably subjected to urban run-off during periods of heavy rain. In some cities, rain water is collected in drains and directed through the sewage collection and treatment facilities before discharge to the river or lake. In other cities, rainwater is channelled directly into the nearest water body. Even where urban run-off is collected in the sewerage system, excessive rainfall can lead to an overload which by-passes the sewage treatment plants. Variables associated with urban run-off are largely the same as those selected for municipal wastewater (Table 3.9). However, water quality problems particularly associated with urban run-off are high levels of oil products and lead (both arising from the use of automobiles), as well as a variety of other metals and contaminants associated with local industrial activity.

Agricultural activities

Impacts relating to agricultural activities principally concern organic and inorganic matter (such as arising from intensive animal rearing and land run-off associated with land clearing) and those chemicals incorporated in fertilisers and pesticides. Irrigation, especially in arid areas, can lead to salinisation of surface and groundwaters and, therefore, inclusion of conductivity, chloride, alkalinity, sulphate, fluoride and sodium is important in water quality assessment programmes in these areas. Suggestions for necessary variables in relation to agricultural activities are given in Table 3.9.

Land disposal of solid municipal and hazardous wastes

In most countries, municipal solid waste is dumped in designated land sites. Similar sites are also used for specific industrial, hazardous wastes which are too toxic to be released to the environment, and are usually sealed in containers. Land disposal sites are often poorly planned and controlled, resulting in the formation of leachates which pose particular risks for groundwaters in the vicinity of the sites (see section 9.4.3). Leachates can contain many contaminants, including pathogens, metals and organic chemicals, depending on the material deposited at the site. Leachates from municipal wastes are usually rich in biodegradable organic matter. Recently, it has been recognised that it is important to include the monitoring of methane in groundwaters close to land waste disposal sites (Table 3.9).

Atmospheric sources

Studies of atmospheric pollutants are constantly increasing the number of variables which need to be included in water quality assessment programmes. Acidic depositions lead to a loss of the acid neutralising capacity or alkalinity, which in turn decreases the pH and affects the normal chemical balance of water bodies. Assessment programmes for lakes in susceptible regions should include alkalinity, pH, sulphate and nitrate (see Table 3.9). Assessment of atmospheric impact with respect to contaminants depends on

local and regional sources of emissions. However, widespread atmospheric transport has been proven for lead, cadmium, arsenic, certain pesticides and other organic compounds.

Industrial effluents and emissions

There are few industries which do not make use of water, either directly as part of the manufactured product or indirectly for cooling, cleaning and circulating. Many of these activities generate liquid effluents which may contain many different chemicals, as well as organic matter, depending on the nature of the industrial processes involved. Assessment programmes for water bodies receiving industrial waste, or close to industrial developments, should include variables selected to indicate background water quality and others selected in relation to the local industrial processes, especially contaminants which may cause harm to the environment or make it unsuitable for other uses. The choice of contaminants should be based on an inventory of the chemicals used and discharged during the industrial processes. Some suggestions of appropriate variables for the principal industrial sectors are given in Table 3.10. When water is polluted as the result of an industrial accident the number of variables to be monitored in the receiving water body may be restricted to those known to be accidentally released (or normally used or produced in the industrial process), together with those physical, chemical and biological variables likely to be affected.

3.12. Summary and recommendations

This chapter provides the basic information necessary to aid selection of appropriate variables for the major types of assessment programmes. These variables should be selected in relation to other methods which may be appropriate, such as analysis of particulate and biological material. The choice of variables will also be influenced by the ability of an organisation to provide the facilities, and suitably trained operators, to enable the selected measurements to be made accurately. Further information on recommended field measurement and laboratory techniques is available in the companion volume to this guidebook by Bartram and Ballance (1996).

The suggested variables for different types of assessment given in Section 3.11 are based on common situations and should be taken as guides only. Full selection of variables must be made in relation to assessment objectives and specific knowledge of each individual situation.

Table 3.10. Selection of variables for the assessment of water quality in relation to some common industrial sources of pollution

	Food processing	Mining	Oil extraction/refining	Chemical/ pharmaceut.	Pulp and paper	Metallurgy	Machine production	Textiles
General variables								
Temperature	x	x	x	x	x	x	x	x
Colour	x	x	x	x	x	x	x	x
Odour	x	x	x	x	x	x	x	x
Residues	x	x	x	x	x	x	x	x
Suspended solids	x	xxx	xxx	x	xxx	xxx	xxx	xxx
Conductivity	xxx	xxx	xxx	x	xxx	xxx	xxx	xxx
pH	xxx	xxx	x	xxx	x	xxx	x	x
Eh	x	x	x	x	x	x	x	x
Dissolved oxygen	xxx	xxx	xxx	xxx	xxx	x	x	xxx
Hardness	x	x	x	x	x	xx	x	x
Nutrients								
Ammonia	xxx	x	xx	xx	x	x	x	x
Nitrate/nitrite	xx	x		xx	x	x		x
Organic nitrogen	xx			x	x			x
Phosphorus compounds	xx			xx			x	x
Organic matter								
TOC	x	x	x	xx	xxx	x	x	x
COD	x	x	x	xxx	xxx	x	x	x
BOD	xxx	x	xxx	xx	xxx	x	x	xxx
Major ions								
Sodium	x	x	x	x				x
Potassium	x	x	x	x				x
Calcium	x	x	x	x	x	xx	x	x
Magnesium	x	x	x	x	x	x		x
Carbonate components	x	x	x	x				
Chloride	xx	xxx	xx	xx	x	x	x	xxx

Sulphate	x	x	xx	xx	xxx	x	x	x
Other inorganic variables								
Sulphide		x	xxx	xxx	xxx	xxx		x
Silica		x	x	x			x	x
Fluoride		x	x	xx		x		x
Boron		x	x	x	x	x	x	x
Cyanide		x		x		x	x	x
Trace elements								
Heavy metals		xxx	xx	xx	x	xxx	xxx	xx
Arsenic		x		x		x		x
Selenium		x		x		x	x	x
Organic contaminants								
Fats	xx							
Oil and hydrocarbons			xxx	xx		xx	xxx	x
Organic solvents				xxx	xxx		x	x
Phenols	x		xx	xxx	xxx	x		x
Pesticides	x			xxx				
Other organics				xxx	xxx	x		
Surfactants	xx		xx	xxx	x	x	x	xx
Microbiological indicators								
Faecal conforms	xxx							
Other pathogens	xxx							

TOC Total organic carbon
COD Chemical oxygen demand
BOD Biochemical oxygen demand

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

3.13. References

AOAC 1990 *Official Methods of Analysis of the Association of Official Analytical Chemists.* 15th edition. Association of Official Analytical Chemists, Washington D.C.

APHA 1989 *Standard Methods for the Examination of Water and Wastewater.* 17th edition, American Public Health Association, Washington D.C., 1,268 pp.

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

Bestemyanov, G.P. and Krotov, Ju.G. 1985 *Maximum Allowable Concentrations of Chemicals in the Environment.* Khimiya, Leningrad, [In Russian].

CEC (Commission of European Communities) 1976 Council Directive of 8 December 1975 concerning the quality of bathing water, (76/160/EEC). *Official Journal,* **L/31,** 1-7.

CEC (Commission of European Communities) 1978 Council Directive of 18 July 1978 on the quality of fresh waters needing protection or improvement in order to support fish life, (78/659/EEC). *Official Journal,* **L/222,** 1-10.

CEC (Commission of European Communities) 1980 Council Directive of 15 July 1980 relating to the quality of water intended for human consumption, (80/778/EEC). *Official Journal,* **L/229,** 23.

Committee for Fisheries 1993 *List of Maximum Allowable Concentrations and Approximately Harmless Levels of Impact of Toxic Chemicals on Water Bodies of Fisheries Importance.* Kolos, Moscow.

Dessery, S., Dulac, C., Lawrenceau, J.M. and Meybeck, M. 1984 Evolution du carbone organique particulaire algal et détritique dans trois rivières du Bassin Parisien. *Arch. Hydrobiol.,* **100** (2), 235-260.

EIFAC (European Inland Fisheries Advisory Commission) 1964 onwards Working Party on Water Quality Criteria for European Freshwater Fish. *Water Quality Criteria for European Freshwater Fish,* EIFAC Technical Paper Series (various titles), Food and Agriculture Organization of the United Nations, Rome.

Environment Canada 1979 *Water Quality Source Book. A Guide to Water Quality Parameters.* Environment Canada, Ottawa, 89 pp.

Environment Canada 1987 *Canadian Water Quality Guidelines* [with updates]. Prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Resource Ministers, Environment Canada, Ottawa.

Gray, N.F. 1994 *Drinking Water Quality. Problems and Solutions.* John Wiley and Sons, Chichester, 315 pp.

Hagebro, C., Bang, S. and Somer, E. 1983 Nitrate/load discharge relationships and nitrate load trends in Danish rivers. *IAHS Publ.* No. **141,** 377-386.

Hem, J.D. 1989 *Study and Interpretation of the Chemical Characteristics of Natural Waters.* Water Supply Paper, 2254, 3rd edition, U.S. Geological Survey. Washington D.C., 263 pp.

ISO 1984 *Water Quality - Determination of the sum of calcium and magnesium - EDTA titrimetric method.* International Standard ISO 6059-1984 (E), First edition 1984-06-01, International Organization for Standardization.

Keith, L.H. 1988 *Principles of Environmental Sampling.* American Chemical Society, 458 pp.

Lorenzen, C.J. 1967 Determination of chlorophyll and phaeopigments: Spectrophotometric equations. *Limnol. Oceanogr.,* **12,** 343-346.

NIH 1987-88 *Physico-chemical Analysis of Water and Wastewater.* National Institute of Hydrology, Roorkee - 247667(UP), India.

Roberts, G. and Marsh, T. 1987 The effects of agricultural practices on the nitrate concentrations in the surface water domestic supply sources of western Europe. In: *Water for the Future: Hydrology in Perspective,* IAHS Publ. No. **164,** 365-380.

Semenov, A.D. [Ed.] 1977 *Guidebook on Chemical Analysis of Inland Surface Waters.* Hydrometeoizdat, Leningrad, 542 pp, [In Russian].

Strickland, J.D.H. and Parsons, T.R. 1972 A practical handbook of seawater analysis. 2nd edition. *Bull. Fish. Res. Bd Canada,* **167,** 310 pp.

US EPA 1993 *Drinking Water Regulations and Health Advisories.* Health and Ecological Criteria Division, United States Environmental Protection Agency, Washington D.C.

Velz, C.J. 1984 *Applied Stream Sanitation.* 2nd edition, John Wiley and Sons, New York, 800 pp.

WHO 1984 *Guidelines for Drinking-Water Quality. Volume 2. Health Criteria and Other Supporting Information.* World Health Organization, Geneva, 335 pp.

WHO 1991 *GEMS/WATER 1990-2000 The Challenge Ahead.* WHO/PEP/91.2, World Health Organization, Geneva.

WHO 1992 *GEMS/Water Operational Guide.* Third edition. World Health Organization, Geneva.

WHO 1993 *Guidelines for Drinking-Water Quality. Volume 1. Recommendations.* Second edition, World Health Organization, Geneva, 188 pp.

WMO 1974 *Guide to Hydrological Practices.* Publication No. 168, World Meteorological Organization, Geneva.

WMO 1980 *Manual on Stream Gauging.* Publication No. 519, World Meteorological Organization, Geneva.