7

WATER QUALITY

LEARNING OBJECTIVES

When you have finished reading this chapter you should have:

■ An understanding of water quality as an issue in hydrology and how it ties into water quantity.
■ A knowledge of the main parameters used to assess water quality and what affects their levels in a river.
■ A knowledge of the measurement techniques and sampling methodology for assessing water quality.
■ A knowledge of techniques used to control water pollution and manage water quality.

This chapter identifies the different types of pollutants that can be found in a river system and describes the major sources of them, especially where elevated levels may be found and what impact their presence has on aquatic ecology. The chapter also outlines the methods used to measure water quality parameters. This is followed with a description of the management techniques used to control water quality in a river catchment.

Traditionally hydrology has been interested purely in the amount of water in a particular area: water quantity. This is frequently referred to as physical hydrology. If, however, we take a wider remit for hydrology – to include the availability of water for human consumption – then issues of water quality are of equal importance to quantity. There are three strong arguments as to why hydrology should consider water quality an area worthy of study.

1 *The interlink between water quality and quantity.* Many water quality issues are directly linked to the amount of water available for dilution and dispersion of pollutants, whether they be natural or anthropogenic in source. It is virtually impossible to study one without the other. An example of this is shown in the Case Study of the River Thames through London (pp. 127–129).

2 *The interlink between hydrological processes and water quality.* The method by which pollutants transfer

from the land into the aquatic environment is intrinsically linked with the hydrological pathway (i.e. the route by which the water moves from precipitation into a stream), and hence the hydrological processes occurring. A good example of this is in Heppell *et al.* (1999) where the mechanisms of herbicide transport from field to stream are linked to runoff pathways in a clay catchment.

3 *Employment of hydrologists.* It is rare for someone employed in water resource management to be entirely concerned with water quantity, with no regard for quality issues. The maintenance of water quality is not just for drinking water (traditionally an engineer's role) but at a wider scale can be for maintaining the **amenity value** of rivers and streams.

It is easy to think of water quality purely in terms of pollution; i.e. waste substances entering a river system as a result of human activity. This is an important issue in water-quality analysis but is by no means the only one. One of the largest water quality issues is the amount of suspended sediment in a river, which is frequently a completely natural process. Suspended sediment has severe implications for the drinking-water quality of a river, but also for other hydrological concerns such as reservoir design and aquatic flora and fauna. As soon as a river is dammed the water velocity will slow down. Simple knowledge of the **Hjulstrom curve** (see Figure 7.1) tells us that this will result in the deposition of suspended sediment. That deposition will eventually reduce the capacity of the reservoir held behind the dam. In high-energy river systems, for even a very large reservoir, a dramatic reduction in capacity can take place within two to four decades. It is critically important for a hydrologist involved in reservoir design to have some feeling for the quantities of suspended sediment so that the lifespan of a reservoir can be calculated. In South Korea, reservoir management includes understanding the sediment plume entering a reservoir during the rainy season and using a multiple level abstraction to release this sediment laden water
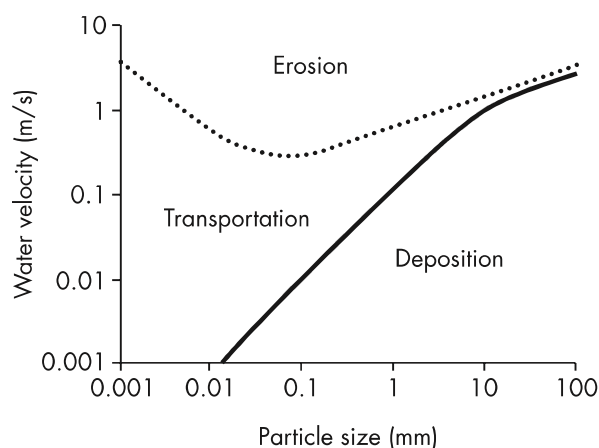

Figure 7.1 The Hjulstrom curve relating stream velocity to the erosion/deposition characteristics for different sized particles (x-axis). In general the slower the water moves the finer the particles that are deposited and the faster the water moves the larger the particles being transported.

during the wet season, i.e. avoiding sedimentation in the dam (Kim *et al.*, 2007).

Spatial variations in water quality may be influenced by many different environmental factors (e.g. climate, geology, weathering processes, vegetation cover and anthropogenic). Often it is a combination of these factors that makes a particular water-quality issue salient for a particular area. An example of this is acid rain (also discussed in Chapter 2) as a particular problem for north-eastern North America and Scandinavia. The sources of the acid rain are fossil-fuel-burning power stations and industry. It becomes a particular problem in these areas for a number of reasons: it is close to the sources of acid rain; high rainfall contributes a lot of acid to the soil; the soils are thin after extensive glaciation and derived from very old rocks; and the soils are heavily leached (have had a lot of water passing through them over a long time period) and have a low buffering capacity (see p. 34). This combination of influences means that the water in the rivers has a low **pH**, and – of particular concern to gill-bearing aquatic fauna – has a high dissolved aluminium content (from the soils).

Having argued for the role of natural water-quality issues to be considered seriously, the reader

Case study

THE RIVER THAMES THROUGH LONDON: WATER QUALITY CHANGE

The River Thames as it flows through London is one of the great tourist sights of Europe. It is an integral part of London, not just for its scenic attraction but also as a transport route right into the heart of a modern thriving city. The river has also a large part to play in London's water resources, both as source of drinking water and a disposal site for waste.

London has a long history of water-quality problems on the Thames, but it has not always been so. Prior to the nineteenth century domestic waste from London was collected in cesspools and then used as fertiliser on agricultural land (hence the use of the term 'sewage farm' for sewage treatment stations). The Thames maintained a fish population, and salmon from the river were sold for general consumption. With the introduction of compulsory water closets (i.e. flushing toilets) in 1843 and the rise in factory waste during the Industrial Revolution, things started to change dramatically for the worse during the nineteenth century. The majority of London's waste went through poorly constructed sewers (often leaking into shallow aquifers which supplied drinking water) straight into the Thames without any form of treatment. In 1854 there was an outbreak of cholera in London that resulted in up to 10,000 deaths. In a famous epidemiological study Dr John Snow was able to link the cholera to sewage pollution in water drawn from shallow aquifers. The culmination of this was 'the year of the great stink' in 1856. The smell of untreated waste in the Thames was so bad that disinfected sheets had to be hung from windows in the Houses of Parliament to lessen discomfort for the lawmakers of the day. In the best NIMBY ('not in my back-yard') tradition this spurred parliament into action and in the following decade, radical changes were made to the way that London used the River Thames. Water abstraction for drinking was only permitted upstream of tidal limits and London's sewage was piped downstream to Beckton where it was discharged (still untreated) into the Thames on an ebb tide.

The result of these reforms was a radical improvement of the river water quality through central London; but there was still a major problem downstream of Beckton. The improvements were not to last, however, as by the middle of the twentieth century the Thames was effectively a dead river (i.e. sustained no fish population and had a dissolved oxygen concentration of zero for long periods during the summer). This was the result of several factors: a rapidly increasing population, increasing industrialisation, a lack of investment in sewage treatment and bomb damage during the Second World War.

Since the 1950s the Thames has been steadily improving. Now there is a resident fish population and migratory salmon can move up the Thames. This improvement has been achieved through an upgrading of the many sewage treatment works that discharge into the Thames and its tributaries. The England and Wales Environment Agency has much to do with the management of the lower Thames and proudly proclaims that the Thames 'is one of the cleanest metropolitan rivers in the world'. How realistic is this claim?

There is no doubt that the Thames has been transformed remarkably from the 'dead' river of sixty years ago into something far cleaner, but there are two problems remaining for the management of the Thames through London, and for one of these nothing can be done.

- The Thames is a relatively small river that does not have the flushing potential of other large rivers; therefore it cannot cleanse itself very easily.

- The sewer network underneath London has not been designed for a large modern city and cannot cope with the strains put on it.

At Westminster (in front of the Houses of Parliament) the Thames is over 300 m wide; this is confined from the width of 800 m evident during Roman times. This great width belies a relatively small flow of fresh water. It appears much larger than in reality because of its use for navigation and the tidal influence. The average flow rate for the Thames is 53 cumecs, rising to 130 cumecs under high flows. In Table 7.1 this is compared with rivers that flow through other major cities. In Seoul, a similar sized capital city, the Han River is over seven times larger than the Thames. The effect of the small flow in the Thames is that it does not have great flushing power. During the summer months it may take a body of water three months to move from west London to the open sea. On each tide it may move up to 14 km in total but this results in less than a kilometre movement downstream. If this body of water is polluted in some way then it is not receiving much dilution or dispersion during the long trip through London.

The second important factor is the poor state of London's sewers. Prior to Sir Joseph Bazalgette's sewer network of 1864 the old tributaries of the Thames acted as sewers, taking waste water directly to the Thames. Bazalgette's grand sewerage scheme intercepted these rivers and transported the sewage through a large pipe to east London. This system still exists today. The actual sewerage network is very well built and still works effectively. The problem is that it is unable to cope with the volume of waste expected to travel through it, particularly when it rains, as it is a combined stormwater–sewage network. The original tributaries of the Thames, such as the Fleet, still exist under London and any storm runoff is channelled into them. When the volume of stormwater and sewage is too great for the sewers the rivers act as overspills and take the untreated sewage directly into the Thames. This is a particular problem during summer storms when the volume of water flowing down the Thames is low and cannot dilute the waste effectively. To combat this problem Thames Water Utilities (part of the private company that treats London's sewage) operate two boats especially designed to inject oxygen directly into the water. These boats can float with a body of sewage-polluted water, injecting oxygen so that the dissolved oxygen level does not reach levels that would be harmful to fish and other aquatic creatures. To help in the tracking of a polluted body of water there are water-quality monitoring stations attached to bridges over the Thames. These stations measure temperature, dissolved oxygen concentration and electrical

Table 7.1 Comparison of rivers flowing through major cities

River	Mean annual flow (m³/s)	City on river or estuary	Population in metropolitan area (million)
Thames	82	London	12.0
Seine	268	Paris	9.93
Hudson	387	New York	19.3
Han	615	Seoul	10.3
Rhine	2,219	Rotterdam	1.1
Paraná/Uruguay	22,000	Buenos Aires	11.6

Source: Flow data from Global Runoff Data Centre

conductivity at fifteen-minute intervals and are monitored by the Environment Agency as they are received in real time at the London office.

In addition to the oxygen-injecting boats, there is tight water-quality management for the River Thames through London. This is operated by the Thames Estuary Partnership, a group of interested bodies including the Environment Agency. Their remit includes other factors such as protecting London from flooding (using the Thames Barrier), but also setting higher effluent standards for sewage treatment works during the summer. The

emphasis is on flexibility in their management of the Thames. There is no question that the River Thames has improved from fifty years ago. In many respects it is a river transformed, but it still has major water-quality problems such as you would expect to find where a small river is the receptacle for the treated waste of over 10 million people. The water-quality management of a river like the Thames needs consideration of many facets of hydrology: understanding pollutants, knowledge of stormflow peaks from large rainfall events, and streamflow statistics.

will find that the majority of this chapter deals with human-induced water-quality issues. This is an inevitable response to the world we live in where we place huge pressures on the river systems as repositories of waste products. It is also important to study these issues because they are something that humans can have some control over, unlike many natural water-quality issues.

Before looking at the water-quality issues of substances within a river system it is worth considering how they reach a river system. In studying water pollution it is traditional to differentiate between *point source* and *diffuse* pollutants. As the terminology suggests, point sources are discrete places in space (e.g. a sewage treatment works) where pollutants originate. Diffuse sources are spread over a much greater land area and the exact locations cannot be specified. Examples of diffuse pollution are excess fertilisers and pesticides from agricultural production. The splitting of pollutants into diffuse and point sources has some merit for designing preventative strategies but like most categorisations there are considerable overlaps. Although a sewage treatment works can be thought of as a point source when it discharges effluent into a stream, it has actually gathered its sewage from a large diffuse area. If there is a particular problem with a sewage treatment works effluent, it may be a result of accumulated diffuse source pollution rather than the actual sewage treatment works itself.

A more useful categorisation of water pollutants is to look at their impacts on the river system. In this way we can differentiate between three major types of pollutants.

- *Toxic compounds*, which cause damage to biological activity in the aquatic environment.
- *Oxygen balance affecting compounds*, which either consume oxygen or inhibit the transfer of oxygen between air and water. This would also include thermal pollution as warm water does not hold as much dissolved oxygen as cold water (see p. 134).
- *Suspended solids* – inert solid particles suspended in the water.

Whether we approve or not, rivers are receptacles for large amounts of waste produced by humans. Frequently this is deliberate and is due to the ability of rivers to cope with waste through degradation, dilution and dispersion. Just how quickly these three processes operate is dependent on the pollutant load already present in the river, the temperature and pH of the water, the amount of water flowing down the river and the mixing potential of the river. The last two of these are river flow characteristics that will in turn be influenced by the time of year, the nature of flow in the river (e.g. the shape of the flow duration curve), and the velocity and turbulence of flow. This demonstrates the strong

interrelationship that exists between water quality and water quantity in a river system.

One remarkable feature about rivers is that given enough time and a reasonable pollution loading, rivers will recover from the input of many pollutant types. That is not to say that considerable harm cannot be done through water pollution incidents, but by and large the river system will recover so long as the pollution loading is temporary. An example of this can be seen in the **oxygen sag curve** (see Figure 7.2) that is commonly seen below point sources of organic pollution (e.g. sewage effluent). The curve shows that upon entering the river there is an instant drop in dissolved oxygen content. This is caused by bacteria and other micro-organisms in the river feeding on the organic matter in the stream and using any available dissolved oxygen. This would have a severe impact on any aquatic fauna unable to move away from this zone of low dissolved oxygen. As the pollutant load moves downstream the degradation, dilution and dispersal starts to take effect and oxygen levels start to recover in the river. The shape of the curve, especially the distance downstream until recovery, is highly dependent on the flow regime of the receiving river. A fast flowing, readily oxygenated stream will recover much faster than a slow-moving river. Large rivers will have a faster recovery time (and the depth of sag will be less) than small streams, due to the amount of dilution occurring.
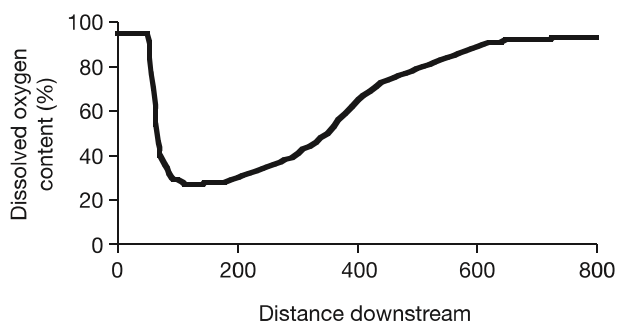

Figure 7.2 Hypothetical dissolved oxygen sag curve. The point at which the curve first sags is the point source of an organic pollutant. The distance downstream has no units attached as it will depend on the size of the river.

WATER-QUALITY PARAMETERS

To analyse the water quality within a river, consideration has to be given to what type of test may be carried out and the sampling pattern to be used. There are numerous parameters that can be measured, and each is important for the part they play in an overall water-quality story. It is not necessary to measure them all for a single water-quality analysis study; instead the relevant parameters for a particular study should be identified. This can be done using a priori knowledge of the water-quality issues being studied. To aid in this, different parameters are discussed here with respect to their source; what type of levels might be expected in natural rivers; and the impact they have on a river ecosystem.

The first distinction that can be made is between physical and chemical parameters. With chemical parameters it is the concentration of a particular chemical substance that is being assessed. With physical parameters it is a physical measurement being made, normally measuring the amount of something within a water sample.

Physical parameters

Temperature

The temperature of water in a river is an important consideration for several reasons. The most important feature of temperature is the interdependence it has with dissolved oxygen content (see p. 134). Warm water holds less dissolved oxygen than colder water. The dissolved oxygen content is critical in allowing aquatic fauna to breathe, so temperature is also indirectly important in this manner. Water temperature is also a controlling factor in the rate of chemical reactions occurring within a river. Warm water will increase the rate of many chemical reactions occurring in a river, and it is able to dissolve more substances. This is due to a weakening of the hydrogen bonds and a greater ability of the bipolar molecules to surround anions and cations.

Warm water may enter a river as thermal pollution from power stations and other industrial processes. In many power stations (gas, coal and nuclear) water is used as a coolant in addition to the generation of steam to drive turbines. Because of this, power stations are frequently located near a river or lake to provide the water source. It is normal for the power stations to have procedures in place so that hot water is not discharged directly into a river; however, despite the cooling processes used, the water is frequently 1–2°C degrees warmer on discharge. The impact that this has on a river system will be dependent on the river size (i.e. degree of dilution and rate of dispersion).

Dissolved solids

In the first chapter, the remarkable ability of water to act as a solvent was described. As water passes through a soil column or over a soil surface it will dissolve many substances attached to the soil particles. Equally water will dissolve particles from the air as it passes through the atmosphere as rain. The amount of dissolved substances in a water sample is referred to as the **total dissolved solids (TDS)**. The higher the level of TDS the more contaminated a water body may be, whether that be from natural or anthropogenic sources. Meybeck (1981) estimates that the global average TDS load in rivers is around 100 mg/l, but it may rise considerably higher (e.g. the Colorado River has an average TDS of 703 mg/l).

Electrical conductivity

A similar measurement to TDS is provided by the electrical conductivity. The ability of a water sample to transmit electrical current (its conductivity) is directly proportional to the concentration of dissolved ions. Pure, distilled water will still conduct electricity but the more dissolved ions in water the higher its electrical conductivity. This is a straight-line relationship, so equation 7.1 can be derived.

$$K = \frac{\text{Conductivity}}{\text{TDS}} \text{ or TDS} = \frac{\text{Conductivity}}{K} \quad (7.1)$$

This relationship gives a very good surrogate measure for TDS. The K term is a constant (usually between 0.55 and 0.75) that can be estimated by taking several measurements of conductivity with differing TDS levels. Conductivity is a simple measurement to take as there are many robust field instruments that will give an instant reading. This can then be related to the TDS level at a later stage. Electrical conductivity is measured in Siemens per metre, although the usual expression is microsiemens per centimetre (μS/cm). Rivers normally have a conductivity between 10 and 1,000 μS/cm.

Suspended solids

The amount of suspended solids has been highlighted at the start of this chapter as a key measure of water quality. The carrying of suspended sediment in a river is part of the natural erosion and sediment transport process. The sediment will be deposited at any stage when the river velocity drops and conversely it will be picked up again with higher river velocities (see Figure 7.1). In this manner the **total suspended solids (TSS)** load will vary in space and time. The amount of TSS in a river will affect the aquatic fauna, because it is difficult for egg-laying fish and invertebrates to breed in an environment of high sediment. Suspended sediment is frequently inert, as in the case of most clay and silt particles, but it can be organic in content and therefore have an oxygen demand.

TSS is expressed in mg/l for a water sample but frequently uses other units when describing sediment load. Table 7.2 shows some values of sediment discharge (annual totals) and calculates an average TSS from the data. It is remarkable to see the data in this form, enabling contrast to be drawn between the different rivers. Although the Amazon delivers a huge amount of sediment to the oceans it has a relatively low average TSS, a reflection of the extremely high discharge. In contrast to this the

Table 7.2 Sediment discharge, total river discharge (averaged over several years) and average total suspended solids (TSS) for selected large river systems

River (country)	Sediment discharge (10^3 tonnes/yr)	Discharge (km^3/yr)	Average TSS (mg/l)
Zaïre (Zaïre)	43,000	1,250	0.03
Amazon (Brazil)	900,000	6,300	0.14
Danube (Romania)	67,000	206	0.33
Mississippi (USA)	210,000	580	0.36
Murray (Australia)	30,000	22	1.36
Ganges-Brahmaputra (Bangladesh)	1,670,000	971	1.72
Huanghe or Yellow (China)	1,080,000	49	22.04

Source: Data from Milliman and Meade (1983)

Huanghe river (sometimes referred to as the Yellow river due to the high sediment load) is virtually a soup! It must be noted that these are average values over a year and that the TSS will vary considerably during an annual cycle (the TSS will rise considerably during a flood).

Turbidity

A similar measure to TSS is the **turbidity**: a measure of the cloudiness of water. The cloudiness is caused by suspended solids and gas bubbles within the water sample, so TSS and turbidity are directly related. Turbidity is measured as the amount of light scattered by the suspended particles in the water. A beam of light of known luminosity is shone through a sample and the amount reaching the other side is measured. This is compared to a standard solution of formazin. The units for turbidity are either FTU (formazin turbidity units) or NTU (normalised turbidity units); they are identical. Turbidity is a critical measure of water quality for the same reasons as TSS. It is a simpler measurement to make, especially in the field, and therefore it is sometimes used as a surrogate for TSS.

Chemical parameters

pH

Chemists think of water as naturally disassociating into two separate ions: the hydroxide (OH^-) and hydrogen (H^+) ions.

$$H_2O \rightleftharpoons OH^- + H^+$$
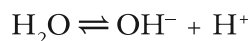
The acidity of water is given by the hydrogen ion, and hence pH (the measure of acidity) is a measure of the concentration of hydrogen ions present. In fact it is the log of the inverse concentration of hydrogen ions (equation 7.2).

$$pH = \log \frac{1}{\left[H^+\right]} \tag{7.2}$$

This works out on a scale between 1 and 14, with 7 being neutral. A pH value less than 7 indicates an acid solution; greater than 7 a basic solution (also called alkaline). It is important to bear in mind that because the pH scale is logarithmic (base 10) a solution with pH value 5 is ten times as acidic as one with pH value 6.

In natural waters the pH level may vary considerably. Rainwater will naturally have a pH value less than 7, due to the absorption of gases such as carbon dioxide by the rainwater. This forms a weak carbonic

acid, increasing the concentration of hydrogen ions in solution. The normal pH of rainfall is somewhere between 5 and 6 but may drop as low as 4, particularly if there is industrial air pollution nearby. For example, Zhao and Sun (1986) report a pH value of 4.02 in Guiyang city, China, during 1982.

Acidic substances may also be absorbed easily as water passes through a soil column. A particular example of this is water derived from peat, which will absorb organic substances. These form organic acids, giving peat-derived water a brown tinge and a low pH value. At the other end of the spectrum rivers that drain carbonate-rich rocks (e.g. limestone and chalk), have a higher pH due to the dissolved bicarbonate ions.

The pH value of rivers is important for the aquatic fauna living within them. The acidity of a river is an important control for the amount of dissolved ions present, particularly metal species. The more acidic a river is the more metallic ions will be held in solution. For fish it is often the level of dissolved aluminium that is critical for their survival in low pH waters. The aluminium is derived from the breakdown of alumino-silicate minerals in clay, a process that is enhanced by acidic water. Water with a pH between 6 and 9 is unlikely to be harmful to fish. Once it drops below 6 it becomes harmful for breeding, and salmonid species (e.g. trout and salmon) cannot survive at a pH lower than 4. Equally a pH higher than 10 is toxic to most fish species (Alabaster and Lloyd, 1980). Table 7.3 summarises the effect of decreasing pH (i.e. increasing acidity) on aquatic ecology.

Mention needs to be made of the confusing terminology regarding **alkalinity**. Alkalinity is a measure of the capacity to absorb hydrogen ions without a change in pH (Viessman and Hammer, 1998). This is influenced by the concentration of hydroxide, bicarbonate or carbonate ions. In water-quality analysis the term 'alkalinity' is used almost exclusively to refer to the concentration of bicarbonate (HCO_3^-) ions because this is the most variable of the three. The bicarbonate ions are derived from the percolation of water through calcareous rocks (e.g. limestones or chalk). It is important to know their concentration for the buffering of pH and for issues of water hardness. The buffering capacity of soils, and water derived from soils, is an important concept in water quality. The buffering capacity of a solution is the ability to absorb acid without changing the pH. This is achieved through a high base cation load or high bicarbonate load. This is why soil derived from limestone and chalk has fewer problems coping with acid rain.

Dissolved oxygen

Dissolved oxygen is vital to any aquatic fauna that use gills to breath. Salmonid species of fish require dissolved oxygen contents greater than 5 mg/l,

Table 7.3 Effect of increasing acidity on aquatic ecology

Effect on organisms or process	pH value
Mayflies disappear	6.5
Phytoplankton species decline – green filamentous periphyton appears	6
Molluscs disappear	5.5–6.0
Waterfowl breeding declines	5.5
Bacterial decomposition slows/fungal decomposition appears	5
Salmonid reproduction fails – aluminium toxicity increases	5
Most amphibia disappear	5
Caddis flies, stone flies and Megaloptera (dobsonflies, alderflies, etc.) disappear	4.5–5.0
Beetles, dragonflies and damselflies disappear	4.5
Most adult fish harmed	4.5

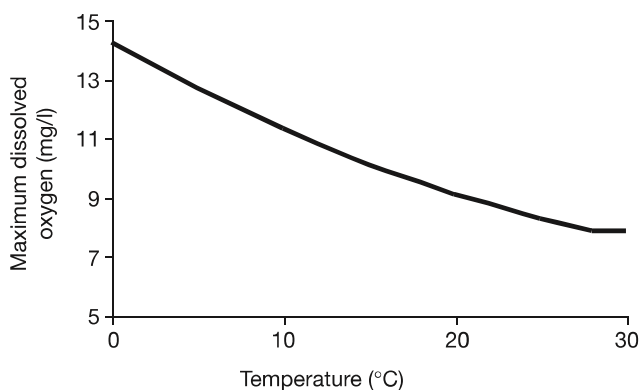*Source*: Dodds (2002), adapted from Jeffries and Mills (1990)

Figure 7.3 Relationship between maximum dissolved oxygen content (i.e. saturation) and temperature.

whereas coarse fish (e.g. perch, pike) can survive in levels as low as 2 mg/l. The dissolved oxygen content is also an important factor in the way we taste water. Water saturated in oxygen tastes fresh to human palates; hence drinking water is almost always oxygenated before being sent through a pipe network to consumers.

There are two methods by which dissolved oxygen content is considered: percentage saturation and concentration (mg/l). These two measures are interrelated through temperature, as the dissolved oxygen content of water is highly temperature dependent (see Figure 7.3).

Biochemical oxygen demand

One of the key water-quality parameters is the five-day biochemical oxygen demand test (sometimes referred to as the **biological oxygen demand** test, or BOD_5). This is a measure of the oxygen required by bacteria and other micro-organisms to break down organic matter in a water sample. It is an indirect measure of the amount of organic matter in a water sample, and gives an indication of how much dissolved oxygen could be removed from water as the organic matter decays.

The test is simple to perform and easily replicable. A sample of water needs to be taken, placed in a clean, darkened glass bottle and left to reach 20°C. Once this has occurred the dissolved oxygen content should be measured (as a concentration). The sample should then be left at 20°C for five days in a darkened environment. After this the dissolved oxygen content should be measured again. The difference between the two dissolved oxygen readings is the BOD_5 value. Over an extended period the dissolved oxygen content of a polluted water sample will look something like that shown in Figure 7.4. In this case the dissolved oxygen content has dropped from 9.0 on day one to 3.6 on day five, giving a BOD_5 value of 5.4 mg/l. After a long period of time (normally more than five days) oxygen will start to be consumed by nitrifying bacteria. In this case the bacteria will be consuming oxygen to turn nitrogenous compounds (e.g. ammonium ions) into nitrate. In order to be sure that nitrifying bacteria are not adding to the oxygen demand a suppressant (commonly allyl thiourea or ATU) is added. This ensures that all the oxygen demand is from the decomposition of organic matter. The use of a five-day period is another safeguard, as, due to the slow growth of nitrifying bacteria, their effect is not noticeable until between eight and ten days (Tebbutt, 1993). There is an argument to be made saying that it does not matter which bacteria are causing the oxygen demand, the test should be looking at all oxygen demand over a five-day period and therefore there is no need to add ATU. However the standard BOD test uses ATU to suppress the nitrifying bacteria.
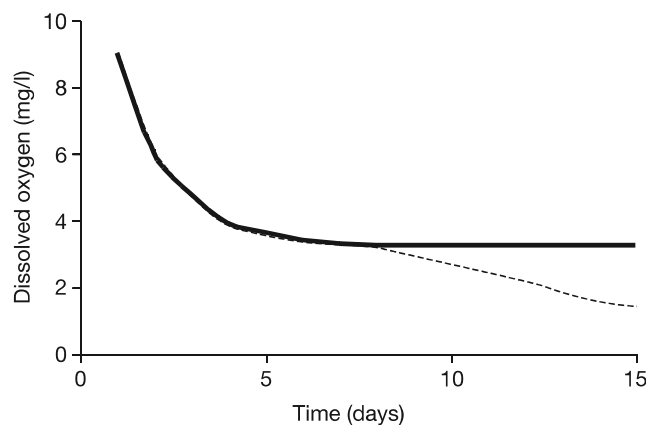

Figure 7.4 Dissolved oxygen curve. The solid line indicates the dissolved oxygen content decreasing due to organic matter. The broken line shows the effect of nitrifying bacteria.

In some cases, particularly when dealing with waste water, the oxygen demand will be higher than total saturation. In this case the sample needs to be diluted with distilled water. The maximum dissolved oxygen content at 20°C is 9.1 mg/l, so any water sample with a BOD_5 value higher than 9 will require dilution. After the diluted test a calculation needs to be performed to find the actual oxygen demand. If you have diluted the sample by half then you need to double your measured BOD_5 value, and so on.

A normal unpolluted stream should have a BOD_5 value of less than 5 mg/l. Untreated sewage is somewhere between 220 and 500 mg/l; while milk has a BOD_5 value of 140,000 mg/l. From these values it is possible to see why a spillage of milk into a stream can have such detrimental effects on the aquatic fauna. The milk is not toxic in its own right, but bacteria consuming the milk will strip the water of any dissolved oxygen and therefore deprive fish of the opportunity to breathe.

There are three reasons why BOD_5 is such a crucial test for water quality:

- Dissolved oxygen is critical to aquatic fauna and the ability to lose dissolved oxygen through organic matter decay is an important measure of stream health.
- It is an indirect measure of the amount of organic matter in the water sample.
- It is the most frequently measured water quality test and has become a standard measure; this means that there are plenty of data to compare readings against.

It also important to realise that BOD is not a direct measure of pollution; rather, it measures the effects of pollution. It also should be borne in mind that there may be other substances present in your water sample that inhibit the natural bacteria (e.g. toxins). In this case the BOD_5 reading may be low despite a high organic load.

Trace organics

Over six hundred organic compounds have been detected in river water, mostly from human activity (Tebbutt, 1993). Examples include benzene, chlorophenols, pesticides, trihalomethanes and polynuclear aromatic hydrocarbons (PAH). These would normally be found in extremely low concentrations but do present significant health risks over the long term. The data for pesticide concentrations (see Table 7.4) in European water resources show that it is a significant problem. This indicates that all water extracted from surface water supplies in Belgium (supplies approximately 30 per cent of the Belgian population) will require pesticide removal before reticulation to customers (Eureau, 2001). Although Germany appears to have no pesticide problem, 10 per cent of its surface water resources occasionally have pesticide levels greater than 0.1 µg/l and 90 per cent have pesticides in concentrations less than 0.1 µg/l (but still present) (Eureau, 2001).

Table 7.4 Percentage of water resources with pesticide concentrations regularly greater than 0.1 µg/l (European Union drinking water standard) for selected European countries

Country	Surface water (%)	Groundwater (%)
Belgium	100	5.2
Denmark	n/a	8.9
Germany	0.0	0.0
Netherlands	50.0	5.0
UK	77.0	6.0

Source: Data from Eureau (2001)

Some of the trace organic compounds accumulate through the food chain so that humans and other species that eat large aquatic fauna may be at risk. Of particular concern are endocrine disrupting chemicals (EDCs), which have been detected in many rivers. These chemicals, mostly a by-product of industrial processes, attack the endocrine system of humans and other mammals, affecting hormone levels. Some chemicals (e.g. DDT) have the ability to mimic the natural hormone oestrogen. Because oestrogen is part of the reproductive process these chemicals have the potential to affect reproductive organs and even DNA. Studies have shown high levels of oestrogen-mimicking compounds in sewage effluent (Montagnani *et al.*, 1996) and that male fish held in cages at sewage effluent discharge sites can develop female sexual organs (Jobling and Sumpter, 1993).

Trace organics can be detected using gas chromatography, although this is made difficult by the sheer number of compounds to be detected. They are removed from drinking water supplies using activated carbon filters, or sometimes oxidation by ozone.

Nitrogen compounds

Nitrogen exists in the freshwater environment in four main forms:

- organic nitrogen – proteins, amino acids and urea
- ammonia – either as free ammonia (NH_3) or the ammonium ion (NH_4^+)
- nitrite (NO_2^-)
- nitrate (NO_3^{2-}).

If organic nitrogen compounds enter a river (e.g. in untreated sewage) then an oxidation process called nitrification takes places. An approximation of the process is outlined below:

$$Organic\ N + O_2 \rightarrow NH_3/NH_4^+ + O_2 \rightarrow NO_2^- + O_2 \rightarrow NO_3^{2-}$$
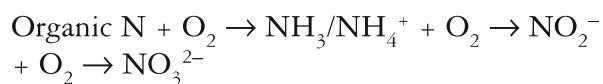
For this to occur there must be nitrifying bacteria and oxygen present. This is one of the main processes operating in a sewage treatment works (see pp. 143–145) – the breakdown of organic nitrogenous compounds into a stable and relatively harmless nitrate. There are two problems with this process occurring in the natural river environment. First, there is the oxygen demand created by the nitrification process. Second, the intermediate ammonia stage is highly toxic, even in very low concentrations. Under extremely low dissolved oxygen concentrations (less than 1 mg/l) the nitrification process can be reversed, at least in the first stage. In this case nitrates will turn into nitrite and oxygen will be released. Unfortunately, this is not a ready means for re-oxygenating a river as by the time the dissolved oxygen level has dropped to 1 mg/l the fish population will have died or moved elsewhere.

The levels of nitrate in a water sample can be expressed in two different ways: absolute nitrate concentration, or the amount of nitrogen held as nitrate (normally denoted as NO_3–N). The two are related by a constant value of approximately 4.4. As an example the World Health Organisation recommended that the drinking water standard for nitrate in drinking water be 45 mg/l. This can also be expressed as 10 mg/l NO_3–N.

As indicated above, one source of nitrate is from treated sewage. A second source is from agricultural fertilisers. Farmers apply nitrate fertilisers to enhance plant growth, particularly during the spring. Plants require nitrogen to produce green leaves, and nitrates are the easiest form to apply as a fertiliser. This is because nitrates are extremely soluble and can easily be taken up by the plant through its root system. Unfortunately this high solubility makes them liable to be flushed through the soil water system and into rivers. To make matters worse a popular fertiliser is ammonium nitrate – $(NH_4)_2NO_3$. This has the added advantage for the farmer of three nitrogen atoms per molecule. It has the disadvantage for the freshwater environment of extremely high solubility and providing ammonium ions in addition to nitrate. The application of nitrate fertilisers is most common in areas of intensive agricultural production such as arable and intensive livestock farming.

Another source of nitrates in river systems is from animal wastes, particularly in dairy farming where slurry is applied to fields. This is organic nitrogen (frequently with high urea content from urine) which will break down to form nitrates. This is part of the nitrification process described earlier.

A fourth source of nitrates in river systems is from plants that capture nitrogen gas from the air. This is not strictly true, as it is actually bacteria such as Rhizobium, attached to a plant's root, that capture the gaseous nitrogen and turn it into water-soluble forms for the plants to use. Not all plants have this ability; in agriculture it is the legumes, such as clovers, lucerne (or alfalfa), peas and soy beans, that can gain nitrogen in this way. Once the nitrogen is in a soluble form it can leach through to a river system in the same way that fertilisers do. Over a summer period the nitrogen levels in a soil build up and then are washed out when autumn and winter rains arrive. This effect is exacerbated by ploughing in the autumn, which releases large amounts of soil-bound nitrogen.

There is one other source of nitrates in rivers: atmospheric pollution. Nitrogen gas (the largest constituent of the atmosphere) will combine with oxygen whenever there is enough energy for it to do so. This energy is readily supplied by combustion engines (cars, trucks, industry, etc.) producing various forms of nitrogen oxide gases (often referred to as NO_x gases). These gases are soluble to water in the atmosphere and form nitrites and nitrates in rainwater. This is not a well-studied area and it is difficult to quantify how much nitrogen reaches rivers from this source (see p. 35).

The different sources of nitrate in a river add together to give a cycle of levels to be expected in a year. Figure 7.5 shows this cycle over a three-year period on the river Lea, south-east England. The low points of nitrate levels correspond to the end of a summer period, with distinct peaks being visible over the autumn to spring period, particularly in the spring. The Lea is a river that has intensive arable agriculture in its upper reaches, but also a significant input from sewage effluent. At times during the summer months the Lea can consist of com-pletely recycled water, and the water may have been through more than one sewage works. This gives a background nitrate level, but it is perhaps surprising that the summer levels of nitrate are not higher, compared to the winter period. Partly this can be attributed to the growth of aquatic plants in the summer, which remove nitrate from the water. The peaks over the autumn–spring period are as a result of agricultural practices discussed above. The example given here is specific to the south-east of England; in different parts of the world the cycles will differ in timing and extent.

Nitrates are relatively inert and do not create a major health concern. An exception to this is methaemoglobinaemina ('blue baby syndrome'). Newborn babies do not have the bacteria in their stomach to deal with nitrates in the same manner as older children and adults. In the reducing surroundings of the stomach the nitrate is transformed into nitrite that then attaches itself to the haemoglobin molecule in red blood cells, preferentially replacing oxygen. This leads to a reduction in oxygen supply around the body, hence the name 'blue baby syndrome'. In reality methaemoglobin-aemina is extremely rare, possibly coming from nitrate-polluted well supplies but not mains-supplied drinking water. The drinking water limit for the European Union is 50 mg/l of nitrate (44 mg/l in the USA). In rivers it is rare to have nitrate values as high as this. In a study of streams draining intensively dairy-farmed land in the North Island of New Zealand, Rodda et al. (1999) report maximum nitrate levels of 26.4 mg/l. These are reported as being 'very high by New Zealand standards' (Rodda et al., 1999: 77). In Figure 7.5 the peak nitrate level for the river Lea in England is 21 mg/l, with the norm being somewhere between 5 and 10 mg/l.

The biggest concern with nitrates in a river system is **eutrophication**. In exactly the same way that the nitrogen enhances the growth of land-based plants, it will also boost the growth of aquatic plants, including algae. This creates a problem of over-production of plant matter in river systems. This is discussed in more detail on pp. 142–143.
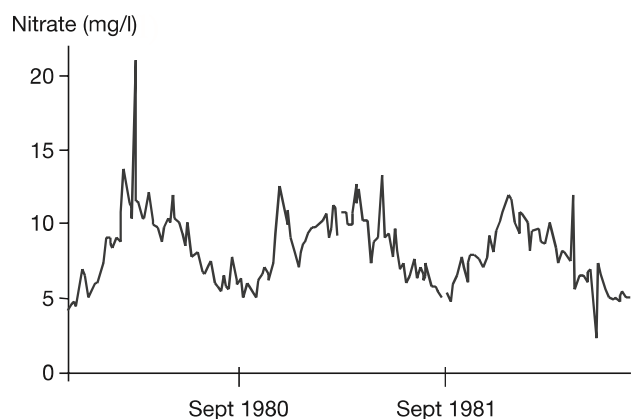
Nitrate (mg/l)

Figure 7.5 Nitrate levels in the river Lea, England. Three years of records are shown: from September 1979 until September 1982.

Source: Data from the Environment Agency

Phosphates

Phosphorus can be found in three different forms: orthophosphate, polyphosphate (both normally dissolved) and organic phosphate (bound to organic particles). The ratio of different forms of phosphorus in a water sample is highly pH dependent (Chapman, 1996). Like nitrogen, the availability of phosphorus is a limiting factor in plant growth. The most common form of application for plants is as phosphate. The major difference from nitrates is that phosphate is not nearly as soluble. Consequently phosphate is normally applied as a solid fertiliser, and less frequently than nitrate. In river systems the main source of dissolved phosphate is from detergents and soaps that come through sewage treatment works. Sewage treatment works remove very little of the phosphate from detergents present in waste water, except where specific phosphate-stripping units are used. The largest amount of phosphate in river systems is normally attached to particles of sediment. Rodda *et al.* (1999) report maximum dissolved reactive phosphorus levels of 0.2 mg/l but total phosphorus levels of 1.6 mg/l. This is for intensive dairy production, where the majority of phosphate is from agricultural fertilisers.

Phosphates are a major contributor to eutrophication problems. The fact that they are bound to sediments means that they often stay in a river system for a long period of time. Improvements in water quality for a river can often be delayed substantially by the steady release of phosphate from sediments on the river bed.

Chlorine

Chlorine is not normally found in river water. It is used as a disinfectant in the supply of drinking water. It is used because it is toxic to bacteria and relatively short lived. More common to find in river water samples is the chloride ion. This may be an indicator of sewage pollution as there is a high chloride content in urine. Chloride ions give the brackish taste of sea water, the threshold for taste being around 300 mg/l. The European Commission limit for drinking water is 200 mg/l.

Heavy metals

'Heavy metals' is the term applied to metals with an atomic weight greater than 6. They are generally only found in very low levels dissolved in fresh water, but may be found in bed load sediments. In acidic waters metals can be dissolved (i.e. found in ionic form). They are often toxic in concentrations above trace levels. The toxicity, in decreasing order, is mercury, cadmium, copper, zinc, nickel, lead, chromium, aluminium and cobalt (Gray, 1999). In the aquatic environment copper and zinc are the most frequent causes of toxicity. A major source of zinc is derived from galvanised steel, particularly in wire fencing and roofs (Alloway and Ayres, 1997).

Accumulation of lead in sediments has been a problem for aquatic wildlife. Since the banning of leaded petrol the major source has been through the use of lead shot and fishing sinkers. Lead shot has been banned in favour of steel shot in many countries (e.g. USA, UK, New Zealand, Australia) due to these problems (Dodds, 2002).

The sources of heavy metals in the aquatic environment are almost always industrial or surface runoff from roads. Sewage sludge (the product of sedimentation at a sewage treatment works) is

frequently heavy metal-rich, derived from industry discharging waste into the sewerage system. When untreated sewage is discharged into a river heavy metals can be found in the sediments. Where there is a combined sewage and storm-water drainage system for an urban area, untreated sewage can be discharged during a storm event when the sewage treatment works cannot cope with the extra storm water. Runoff from roads (through a stormwater system) frequently shows high levels of copper from vehicle brake pads. When washed into a river system, particularly in summer storms, the copper levels can be extremely high and cause toxicity problems to aquatic fauna.

WATER-QUALITY MEASUREMENT

The techniques used for water-quality analysis vary considerably depending on equipment available and the accuracy of measurement required. For the highest accuracy of measurement water samples should be taken back to a laboratory, but this is not always feasible. There are methods that can be carried out in the field to gain a rapid assessment of water quality. Both field and laboratory techniques are discussed on the following pages. Before discussing the measurement techniques it is important to consider how to sample for water quality.

Sampling methodology

It is difficult to be specific on how frequently a water sample should be taken, or how many samples represent a given stretch of water. The best way of finding this out is to take as many measurements as possible in a trial run. Then statistical analyses can be carried out to see how much difference it would have made to have had fewer measurements. By working backwards from a large data set it is possible to deduce how few measurements can be taken while still maintaining some accuracy of overall assessment. An example of this type of approach,

when used for the reduction in a hydrometry (water quantity) network, is in Pearson (1998). The main concern is that there are enough measurements to capture the temporal variability present and that the sample site is adequately representative of your river stretch.

One important consideration that needs to be understood is that the sample of water taken at a particular site is representative of all the catchment above it, not just the land use immediately adjacent. Adjacent land use may have some influence on the water quality of a sample, but this will be in addition to any affect from land uses further upstream which may be more significant.

Gravimetric methods

Gravimetric analysis depends on the weighing of solids obtained from a sample by evaporation, filtration or precipitation (or a combination of these three). This requires an extremely accurate weighing balance and a drying oven, hence it is a laboratory technique rather than a field one. An example of gravimetric analysis is the standard method for measuring total dissolved solids (TDS). This is to filter a known volume of water through 0.45 μm (1 micron = one-millionth of a metre or one-thousandth of a millimetre) filter paper. The sample of water is then dried at 105°C and the weight of residue left is the TDS.

Other examples of gravimetric analysis are total suspended solids and sulphates (causing a precipitate and then weighing it).

Volumetric methods

Volumetric analysis is using titration techniques to find concentrations of designated substances. It is dependent on measuring the volume of a liquid reagent (of known concentration) that causes a visible chemical reaction. This is another laboratory technique as it requires accurate measurements of volume using pipettes and burettes. Examples of this technique are chloride and dissolved oxygen (using the Winkler method).

Colorimetry

Colorimetric analysis depends on a reagent causing a colour to be formed when reacting with the particular ion you are interested in measuring. The strength of colour produced is assumed to be proportional to the concentration of the ion being measured (Beer's law). The strength of colour can then be assessed using one of four techniques: comparison tubes, colour discs, colorimeter or spectrophotometer.

Comparison tubes are prepared by using standard solutions of the ion under investigation which the reagent is added to. By having a range of standard solutions the strength of colour can be compared (by eye) to find the concentration of the water sample. The standard solutions will fade with time and need remaking, hence this is a time-consuming method.

Colour discs use the same principle as comparison tubes, except in this case the standards are in the form of coloured glass or plastic filters. The coloured sample is visually compared to the coloured disc to find the corresponding concentration. It is possible to buy colour disc kits that come with small packets of reagent powder for assessment of a particular ion. This method is extremely convenient for rapid field assessment, but is subjective and prone to inaccuracy.

A colorimeter (sometimes called an absorptiometer) takes the subjective element out of the assessment. It is similar to a turbidity meter in that a beam of light is shone through the reagent in a test tube. The amount of light emerging from the other side is detected by a photo-electric cell. The darker the solution (caused by a high concentration of reactive ion) the less light emerges. This reading can then be compared against calibrations done for standard solutions.

A spectrophotometer is the most sophisticated form of colorimetric assessment. In this case instead of a beam of white light being shone through the sample (as for the colorimeter) a specific wavelength of light is chosen. The wavelength chosen will depend on the colour generated by the reagent and is specified by the reagent's manufacturer.

There are a range of spectrophotometers available to perform rapid analysis of water quality in either a laboratory or field situation. Many ions of interest in water-quality analysis can be assessed using colorimetric analysis. These include nitrate, nitrite, ammonia and phosphate.

Ion-selective electrodes

In a similar vein to pH meters ion-selective electrodes detect particular ions in solution and measure the electrical potential produced between two reactive substances. The tip of the electrode in the instrument has to be coated with a substance that reacts with the selected ion. With time the reactive ability of the electrode will decrease and need to be replaced. Although convenient for field usage and accurate, the constant need for replacing electrodes makes these an expensive item to maintain. There are ion-selective electrodes available to measure dissolved oxygen, ammonium, nitrate, calcium, chloride and others.

Spectral techniques

When ions are energised by passing electricity through them, or in a flame, they produce distinctive colours. For instance, sodium produces a distinctive yellow colour, as evidenced by sodium lamps used in some cars and street lamps. Using spectral analysis techniques the light intensity of particular ions in a flame are measured and compared to the light intensity from known standard solutions. The most common form of this analysis is atomic absorption spectrophotometry, a laboratory technique which is mostly used for metallic ions.

PROXY MEASURES OF WATER QUALITY

Any measurement of water quality using individual parameters is vulnerable to the accusation that it represents one particular point of time but not the

overall water quality. It is often more sensible to try and assess water quality through indirect measurement of something else that we know is influenced by water quality. Two such proxy measures of water quality are provided by biological indicators and analysis of sediments in the river.

Biological indicators

Aquatic fauna normally remain within a stretch of water and have to try and tolerate whatever water pollution may be present. Consequently the health of aquatic fauna gives a very good indication of the water quality through a reasonable period of time. There are two different ways that this can be done: catching fauna and assessing their health; or looking for the presence and absence of key indicator species.

Fish surveys are a common method used for assessing the overall water quality in a river. It is an expensive field technique as it requires substantial human resources: people to wade through the water with electric stun guns and then weigh and measure stunned fish. When this is done regularly it gives very good background information on the overall water quality of a river.

More common are biological surveys using indicator species, particularly of macro-invertebrates. Kick sampling uses this technique. A bottom-based net is kicked into sediment to catch any bottom-based macro-invertebrates, which are then counted and identified. There are numerous methods that can be used to collate this species information. In Britain the BMWP (Biological Monitoring Working Party) score is commonly used and provides good results. Species are given a score ranging from 1 to 10, with 10 representing species that are extremely intolerant to pollution. The presence of any species is scored (it is purely presence/absence, not the total number) and the total for the kick sample calculated. The BMWP score has a maximum of 250. Other indicator species scores include the Chandler index and the ASPT (Average Score Per Taxon). Details of these can be found in a more detailed water-quality assessment text such as Chapman (1996).

Another example of an indicator species used for water-quality testing is *Escherichia coli* (*E. coli*). These are used to indicate the presence or absence of faecal contamination in water. *E. coli* is a bacteria present in the intestines of all mammals and excreted in large numbers in faeces. Although one particular strain (*E. coli*$_{157}$) has toxic side effects the vast majority of *E. coli* are harmless to humans. Their presence in a water sample is indicative of faecal pollution, which may be dangerous because of other pathogens carried in the contaminated water. They are used as an indicator species because they are easy to detect, while viruses and other pathogens are extremely difficult to measure. Coliform bacteria (i.e. bacteria of the intestine) are detected by their ability to ferment lactose, producing acid and gas (Tebbutt, 1993). There are specific tests to grow *E. coli* in a lactose medium, which allow the tester to derive the most probable number per 100 ml (MPN/100 ml).

Sediments

The water in a channel is not the only part of a river that may be affected by water pollution. There are many substances that can build up in the sediments at the bottom of a river and provide a record of pollution. There are two big advantages to this method for investigating water quality: the sediments will reflect both instantaneous large pollution events and long, slow contamination at low levels; and if the river is particularly calm in a certain location the sediment provides a record of pollution with time (i.e. depth equals time). Not all water pollutants will stay in sediments, but some are particularly well suited to study in this manner (e.g. heavy metals and phosphorus).

The interpretation of results is made difficult by the mobility of some pollutants within sediments. Some metals will bind very strongly to clay particles in the sediments (e.g. lead and copper), and you can be fairly certain that their position is indicative of where they were deposited. Others will readily disassociate from the particles and move around in the interstitial water (e.g. zinc and cadmium)

(Alloway and Ayres, 1997). In this case you cannot be sure that a particularly high reading at one depth is from deposition at any particular time.

MODELLING WATER QUALITY

The numerical modelling of water quality is frequently required, particularly to investigate the effects of particular water-quality scenarios. The type of problems investigated by modelling are: the impact of certain levels of waste discharge on a river (particularly under low flow levels); recovery of a water body after a pollution event; the role of backwaters for concentration of pollutants in a river; and many more. The simplest water-quality models look at the concentration of a certain pollutant in a river given knowledge about flow conditions and decay rates of the pollutant. The degradation of a pollutant with time can be simulated as a simple exponential decay rate equation. A simple mass balance approach can then be used to calculate the amount of pollutant left in the river after a given period of time (James, 1993). More complex models build on this approach and incorporate ideas of diffusion, critical loads of pollutants and chemical reaction between pollutants in a river system. If the problem being researched is to track pollutants down a river then it is necessary to incorporate two- or three-dimensional representation of flow hydraulics. There are numerous water-quality models available in the research literature, as well as those used by consultants and water managers.

EUTROPHICATION

'Eutrophication' is the term used to describe the addition of nutrients to an aquatic ecosystem that leads to an increase in net primary productivity. The term comes from limnology (the study of freshwater bodies, e.g. lakes and ponds) and is part of an overall classification system for the nutrition, or trophic, level of a freshwater body. The general classification moves from oligotrophic (literally 'few nutrients'),

to eutrophic ('good nutrition') and ends with hypertrophic ('excess nutrients'). In limnology this classification is viewed as part of a natural progression for bodies of water as they fill up with sediment and plant matter. Eutrophication is a natural process (as part of the nitrogen and phosphorus cycles), but it is the addition of extra nutrients from anthropogenic activity that attracts the main concern in hydrology. In order to distinguish between natural and human-induced processes the term 'cultural eutrophication' is sometimes used to identify the latter.

The major nutrients that restrict the extent of a plant's growth are potassium (K), nitrogen (N) and phosphorus (P). If you buy common fertiliser for a garden you will normally see the K:N:P ratio expressed to indicate the strength of the fertiliser. For both aquatic and terrestrial plants nitrogen is required for the production of chlorophyll and green leaves, while potassium and phosphorus are needed for root and stem growth. In the presence of abundant nitrogen and phosphorus (common water pollutants, see pp. 136–138), aquatic plant growth, including algae, will increase dramatically. This can be seen as positive as it is one way of removing the nitrate and phosphate from the water, but overall it has a negative impact on the river system. The main negative effect is a depletion of dissolved oxygen caused by bacteria decomposing dead vegetative matter in the river. In temperate regions this is a particular problem in the autumn when the aquatic vegetation naturally dies back. In tropical regions it is a continual problem. A second negative effect is from algal blooms. In 1989 there was an explosion in cyano-bacteria numbers in Rutland Water, a reservoir supplying drinking water in central England (Howard, 1994). (NB These are also called blue-green algae, despite being a species of cyano-bacteria.) The cyano-bacteria produce toxins as waste products of respiration that can severely affect water quality. In the 1989 outbreak several dogs and sheep that drank water from Rutland Water were poisoned, although no humans were affected (Howard, 1994). In an effort to eliminate future problems the nutrient-rich source water for Rutland

Water is supplemented with water from purer river water pumped from further afield.

Eutrophication of water can occur at what appear to be very low nutrient levels. As an example the drinking water standard for nitrate-nitrogen is around 12 mg/l (depending on country) but concentrations as low as 2–3 mg/l can cause eutrophication problems in water bodies.

Table 7.5 shows some of the indicators used in a quantitative example of defined trophic levels developed for the Organisation for Economic Co-operation and Development (OECD). The chlorophyll is an indicator of algal growth in the water, while phosphorus and dissolved oxygen are more traditional water-quality measures. The dissolved oxygen is taken from the bottom of the lake because this is where the vegetative decomposition is taking place. The dissolved oxygen level near to the surface will vary more because of the proximity to the water/air interface and the oxygen produced in photosynthesis by aquatic plants. It is worth noting that heavily eutrophied water samples will sometimes have a dissolved oxygen greater than 100 per cent. This is due to the oxygen being produced by algae which can supersaturate the water.

CONTROLLING WATER QUALITY

Waste water treatment

The treatment of waste water is a relatively simple process that mimics natural processes in a controlled, unnatural environment. The treatment processes used for industrial waste water is dependent on the type of waste being produced. In this section the processes described are those generally found in sewage treatment rather than in specialised industrial waste water treatment.

There are two major objectives for successful sewage treatment: to control the spread of disease from waste products and to break down the organic waste products into relatively harmless metabolites (i.e. by-products of metabolism by bacteria, etc.). The first objective is achieved by isolating the waste away from animal hosts so that viruses and other pathogens die. The second objective is particularly important for the protection of where the treated effluent ends up – frequently a river environment.

In Britain the first attempt to give guidelines for standards of sewage effluent discharge were provided by the Royal Commission on Sewage Disposal which sat between 1898 and 1915. The guidelines are based on two water-quality parameters described earlier in this chapter: suspended solids and biochemical oxygen demand (BOD). The Royal Commission set the so-called 30:20 standard which is still applicable today (i.e. 30 mg/l of suspended solids and 20 mg/l of BOD). The standard was based on a dilution ratio of 8:1 with river water. Where river flow is greater than eight times the amount of sewage effluent discharge the effluent should have a TSS of less than 30 mg/l and a BOD of less than 20 mg/l. There was also the recommendation that if the river is used for drinking water extraction further downstream the standard should be tightened to 10:10. This was

Table 7.5 OECD classification of lakes and reservoirs for temperate climates

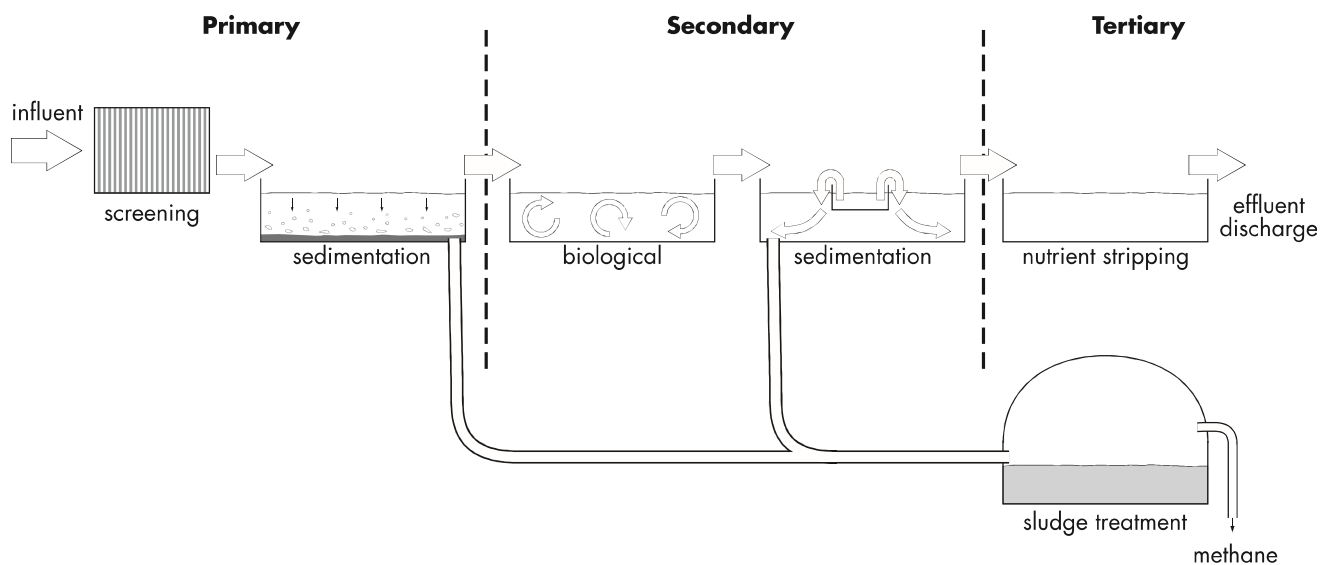| Trophic level	Average total P (mg/l)	Dissolved oxygen (% saturation)	Max. chlorophyll (mg/l) (at depth)
Ultra-oligotrophic	0.004	>90	0.0025
Oligotrophic	0.01	>80	0.008
Mesotrophic	0.01–0.035	40–89	0.008–0.025
Eutrophic	0.035–0.1	0–40	0.025–0.075
Hypertrophic	>0.1	0–10	>0.075

Source: Adapted from Meybeck *et al.* (1989)

Figure 7.6 Schematic representation of waste water treatment from primary through to tertiary treatment, and discharge of the liquid effluent into a river, lake or the sea.

used as a recommendation until the 1970s when a system of legal consents to discharge was introduced (see p. 147).

The processes operating at a waste water treatment works are very simple. They are summarised below and in Figure 7.6 (NB not every sewage treatment works will have all of these processes present).

1 Primary treatment: screening and initial settlement.
2 Secondary treatment: encouraging the biological breakdown of waste and settling out of remaining solids. This can take place either in trickle bed filters or activated sludge tanks. The main requirement is plenty of oxygen to allow micro-organisms to break down the concentrated effluent.
3 Tertiary treatment: biodigestion of sludge (from earlier settling treatment); extra treatment of discharging effluent to meet water-quality standards (e.g. phosphate stripping, nitrate reduction).

Raw sewage entering a sewage treatment works is approximately 99.9 per cent water (Gray, 1999). This is derived from water used in washing and toilet flushing, and also from storm runoff in an urban environment where there is a combined sewage/stormwater drainage scheme. Of the solids involved, the majority are organic and about half are dissolved in the water (TDS). Of the organic compounds the breakdown is approximately 65 per cent nitrogenous (proteins and urea), 25 per cent carbohydrates (sugars, starches, cellulose) and 10 per cent fats (cooking oils, grease, soaps) (Gray, 1999). Typical values for TSS and BOD at different stages of sewage treatment are provided in Table 7.6.

In tertiary treatment an effort is sometimes (but not always) made to reduce the level of nitrate and phosphorus in the discharged waste. In some cases this is achieved through final settling ponds where the growth of aquatic flora is encouraged and the nutrients are taken up by the plants before discharge into a stream. Of particular use are reeds which do not die back during the winter (in temperate regions). This is a re-creation of natural wetlands that have been shown to be extremely efficient removers of both nitrogen and phosphorus from streams (e.g. Russel and Maltby, 1995). Other methods of phosphate removal are to add a lime or metallic salt coagulant that causes a chemical

Table 7.6 Changes in suspended solids and biochemical oxygen demand through sewage treatment. These are typical values which will vary considerably between treatment works

Stage of treatment	Suspended solids (mg/l)	BOD (mg/l)
Raw sewage	400	300
After primary treatment	150	200
After biological treatment	300	20
Effluent discharged to river	30	20

reaction with the dissolved phosphorus so that an insoluble form of phosphate settles out. This is particularly useful where the receiving water for the final effluent has problems with eutrophication. The average phosphorus concentration in raw sewage is 5–20 mg/l, of which only 1–2 mg/l is removed in biological treatment.

In some cases, particularly in the USA, chlorination of the discharging effluent can take place. Chlorine is used as a disinfectant to kill any pathogens left after sewage treatment. This is a noble aim but creates its own difficulties. The chlorine can attach to organic matter left in the effluent and create far worse substances such as polychlorinated biphenyl (PCB) compounds. Another safer form of disinfection is to use ultraviolet light, although this can be expensive to install and maintain.

Source control

The best way of controlling any pollution is to try and prevent it happening in the first place. In order to achieve this differentiation has to be made between point source and diffuse pollutants (see p. 129). When control over the source of pollutants is achieved dramatic improvements in river-water quality can be achieved. An example of this is shown in the Case Study of the Nashua River in Massachusetts, USA.

Case study

CONTROLLING WATER QUALITY OF THE NASHUA RIVER

The Nashua river is an aquatic ecosystem that has undergone remarkable change in the last one hundred years. It drains an area of approximately 1,400 km² in the state of Massachusetts, USA, and is a tributary of the much larger Merrimack river which eventually flows into the sea in Boston Harbor (see Figure 7.7). The land use of the Nashua catchment is predominantly forest and agricultural, with a series of towns along the river. It is the industry associated with these towns that has brought about the changes in the Nashua, predominantly through the twentieth century.

The latter-day changes are well illustrated by the two photographs at the same stretch of the Nashua, in 1965 and 1995 (see Plates 9 and 10).

Prior to European colonisation of North America the Nashua valley was home to the Nashaway tribe, and the Nashua river could be considered to be in a pristine condition. With the arrival of European settlers to New England the area was used for agriculture and the saw milling of the extensive forests. The Industrial Revolution of the nineteenth century brought manufacturing to the area and mills sprang up along the river. By

the middle of the twentieth century the small towns along the Nashua (Gardner, Fitchburg, Leominster and Nashua) were home to paper, textile and shoe factories, many of which were extracting water from the river and then discharging untreated waste back into the river. The photograph of the Nashua in 1965 (Plate 9) is indicative of the pollution problems experienced in the river; in this case dye from a local paper factory has turned the river red. Under the US water-quality classification scheme the river was classified as U: unfit to receive further sewage.

In 1965 the Nashua River Clean-Up Committee was set up to try to instigate a plan of restoring the water quality in the river. This committee later became the Nashua River Watershed Association (NRWA) which still works today to improve water-quality standards in the area. Between 1972 and 1991 eleven waste water-treatment plants were constructed or upgraded to treat waste from domestic, and to a lesser extent from industrial, sources in the catchment. These were built using grants from the state and federal government as part of a strategy to improve the river from U to B status (fit for fishing and swimming). Through this control of point source pollution the river-water quality has improved dramatically as can be seen in the second photograph of the river (Plate 10). The river has attained B status and is an important recreational asset for the region. It has not returned to a pristine state, though, and is unlikely to while there is still a significant urban population in the catchment. There are problems with combined sewage and stormwater drainage systems discharging untreated waste into the river

during large storms, and also diffuse pollution sources – particularly in the urban environment. However, during the latter half of the twentieth century the Nashua river has had its water quality transformed from an abiotic sewer into a clean

Figure 7.7 Location of the Nashua catchment in north-east USA.

river capable of maintaining a healthy salmonid fish population. This has largely been achieved through the control of point pollution sources.

The author gratefully acknowledges the Nashua River Watershed Association for supplying much of this information and Plates 9 and 10. For more information on the NRWA visit: http://www.nashuariverwatershed.org/

Controlling point source pollutants

The control of point source pollutants cannot always be achieved by removing that point source. It is part of water resource management to recognise that there may be valid reasons for disposing of waste in a river; effective management ensures that waste

disposal creates no harmful side effects. In the United Kingdom the control of point source pollution is through discharge consents. These provide a legal limit for worst-case scenarios – for example, at individual sewage treatment works they are usually set with respect to TSS, BOD and ammonia (sometimes heavy metals are included), and calculated to allow

Technique: Calculating discharge consents

In England and Wales the setting of discharge consents for point source pollution control is carried out by the Environment Agency. A discharge consent gives a company the right to dispose of a certain amount of liquid waste into a river system so long as the pollution levels within the discharge are below certain levels. To calculate what those critical levels are a series of computer programs are used. These computer programs are in the public domain and can be obtained from the Environment Agency. They use very simple principles that are described here.

The main part of the discharge consent calculation concentrates on a simple mass balance equation (7.3):

$$C_D = \frac{Q_U C_U + Q_E C_E}{Q_B + Q_E} \qquad (7.3)$$

where Q refers to the amount of flow (m³/s) and C the concentration of pollutant. For the subscripts: D is for downstream; U is for upstream (i.e. the background); and E is for the effluent.

With this mass balance equation the downstream concentration can be calculated with varying flows and levels of effluent concentrations. This variation in flow and concentration is achieved through a computer program running a Monte Carlo simulation.

In this case the Monte Carlo simulation involves a random series of values for Q_U, Q_E, C_U and C_E drawn from an assumed distribution for each variable. It is assumed that the distributions are log-normal in shape (see Figure 7.8) and therefore using the data in Table 7.7 the actual distribution for each variable is simulated. Once the distribution for each variable is known then a random variable is chosen from that distribution. In the case of a log-normal distribution this means that it is most likely to be close to the mean value but more likely to be above than below the mean (see Figure 7.8). In a Monte Carlo simulation the
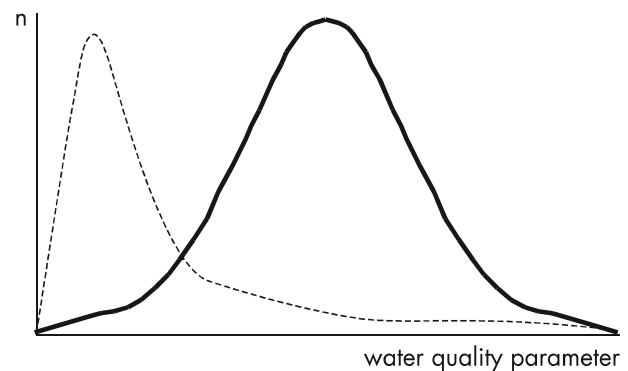

Figure 7.8 A log-normal distribution (broken line) compared to a normal distribution (solid line).

value of C_D is calculated many times (often set to 1,000) so that a distribution for C_D can be drawn. The consent to discharge figure is taken from the distribution of C_D, usually looking at the 90 or 95-percentile values, i.e. the target will be achieved 90 or 95 per cent of the time.

Table 7.7 Parameters required to run a Monte Carlo simulation to assess a discharge consent

Variable	Required data
River flow (Q_U)	Mean daily flow and Q_{95}
Upstream river quality (C_U)	Mean value and standard deviation
Effluent flow (Q_E)	Mean value and standard deviation
Effluent quality (C_E)	Mean and standard deviation

The values that are required for calculating a consent to discharge (see Table 7.7) are derived from normal hydrological data. River flow data can be derived from a flow duration curve (see Chapter 6). The water quality information requires at least three to four years of regular measurements. The values to describe Q_E and C_E will either be known or are to be varied in the simulation in order to derive a consent to discharge value.

In short, the person calculating the discharge consent inserts values from Table 7.7 into the Monte Carlo simulation. This will then produce the 95 percentile value of C_D. If that value is too high (i.e. too much pollution) then the simulation is run again using lower values for C_E until a reasonable value is derived. Once the reasonable value has been reached then the 95 percentile value of C_E is taken as the discharge consent. The definition of a 'reasonable value' will be dependent on the designated use of the river. Rivers with high-class fisheries and those with abstraction for potable supply have much higher standards than for other uses.

The approach described here can be used to calculate a consent to discharge for such water quality parameters as BOD and TSS. When a calculation is being carried out for ammonia then more data are required to describe the water quality in the receiving river. Parameters such as pH, temperature, alkalinity, TDS and dissolved oxygen (all described with mean and standard deviation values) are required so that chemical reaction rates within the river can be calculated.

A scheme such as discharge consents provides a legal framework for the control of point source pollutants but the actual control comes about through implementing improved waste water treatment.

for low flow levels in the receiving stream (see the technique box for calculating discharge consents on p. 147). There is also an obligation to comply with the European Union Urban Waste Water directive.

Controlling diffuse source pollutants

The control of diffuse source water pollution is much harder to achieve. In an urban environment this can be achieved through the collection of storm-water drainage into artificial wetlands where natural processes can lessen the impact of the pollutants on the draining stream. Of particular concern is runoff derived from road surfaces where many pollutants are present as waste products from vehicles. Hamilton and Harrison (1991) suggest that although roads only make up 5–8 per cent of an urban catchment area they can contribute up to 50 per cent of the TSS, 50 per cent of the total hydrocarbons and 75 per cent of the total heavy metals input into a stream. The highest pollutant loading comes during long, dry periods which may be broken by flushes of high rainfall (e.g. summer months in temperate regions). In this case the majority of pollutants reach the stream in the first flush of runoff. If this runoff can be captured and held then the impact of these diffuse pollutants is

lessened. This is common practice for motorway runoff where it drains into a holding pond before moving into a nearby water course.

Another management tool for control of diffuse pollutants is to place restrictions on land management practices. An example of this is in areas of England that have been designated either a Nitrate Vulnerable Zone (NVZ) or a Nitrate Sensitive Area (NSA), predominantly through fears of nitrate contamination in aquifers. In NSAs the agricultural practices of muck spreading and fertilising with nitrates are heavily restricted. This type of control relies on tight implementation of land use planning – something that is not found uniformly between countries, or even within countries.

Examples of controlling water pollution

Biggs (1989) presents data showing the recovery of a river in New Zealand following effective treatment of a point source pollution problem. The pollution was due to discharge of untreated effluent from an abattoir, directly into a nearby branch of the Waimakariri river. Water quality was monitored upstream and downstream of the discharge point before and after a staged improvement in wastewater treatment at the abattoir. The results shown in

Figure 7.9 use an autotrophic index, a ratio of the periphyton mass to the chlorophyll-a. This is a measure of the proportions of heterotrophic (require organic carbon to survive) to autotrophic (produce organic compounds from simple molecules) organisms. The time series of data upstream and downstream from the abattoir (Figure 7.9) can be split between the pre-treatment (Sep–Oct 1985), the recovery period (May–Aug 1986) and the recovered period (after August 1986) (Biggs, 1989). (NB the vertical axis is on a logarithmic scale so differences appear smaller.) A remarkable point about this study is how quickly the river appears to have recovered (approximately five months) following treatment of the point source pollution. This is a reflection of the low residence time of the pollutants within the river system and the effective flushing out of the pollutants by the river.

Dodds (2002) presents two case studies on lake eutrophication with varying degrees of success. The first is for Lake Washington on the eastern border of Seattle, USA. For Lake Washington the diversion of treated sewage away from the lake (achieved in 1963) was enough to halt the decline in water quality and return the lake to an oligotrophic state. For Lake Trummen in Sweden the stopping of sewage input into the lake was n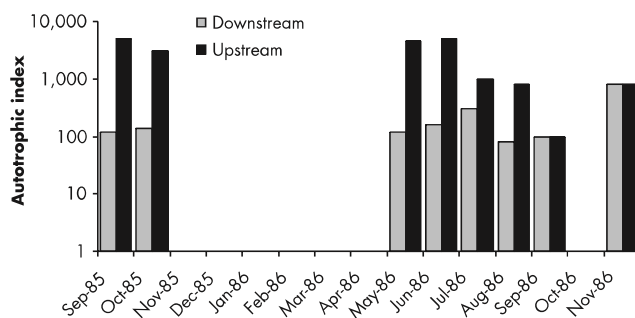ot enough to improve water quality since high levels of phosphorous remained in the lake sediment continuing the eutrophication problem. In this case a dramatic rise in water quality was achieved by dredging the lake sediments (and selling the dredged sediments as nutrient topsoil) so that the lake was able to be returned to recreational usage (Dodds, 2002).

In New Zealand there is an ongoing study to improve the water quality in Lake Rotorua in the Central North Island. This is a lake of tremendous importance for tourism and of great cultural importance to the local Māori people. Initially it was thought that the water quality problem could be solved through treating the point source pollution at a sewage treatment plant which received a significant upgrade in 1990. Although this caused a temporary decrease in nutrient loading to the lake the water quality has continued to decline, largely due to agricultural intensification in the lake catchment area. Nitrate-nitrogen levels in the streams feeding into the lake are in the order of 1–2 mg/l but have increased significantly over the past thirty years (White et al., 2007). A major concern is that the groundwater levels of nitrate-nitrogen are higher than this, effectively delaying the movement of nutrient to the lake but also making restoration of the lake a very long-term project. Planned action for improving Lake Rotorua water quality include diverting a spring-fed stream away from the lake and buying up intensively farmed land to change the land use to low input forest (White et al., 2007). These are expensive options that will take many years to implement and for which it will take even longer to see the results.

Figure 7.9 Recovery in water quality after improved waste water treatment at an abattoir. The waste water treatment was implemented with progressive reductions in effluent discharged into the river from May 1986. See text for explanation of vertical axis.

Source: Redrawn from Biggs (1989)

SUMMARY

The measurement and management of water quality in a river is an important task within hydrology. To carry this out, a knowledge of the pollution type, pollution source (assuming it is not natural) and pathways leading into the stream are important. Equally, it is important to know the flow regime of any receiving river so that dilution rates can be

assessed. There are methods available to control water quality, whether through treatment at point sources (e.g. waste water treatment) or control throughout a catchment using land use planning.

ESSAY QUESTIONS

1   **Explain the Hjulstrom curve and describe its importance for suspended loading in a river.**

2   **Discuss the importance of the BOD$_5$ test in the assessment of overall water quality for a river.**

3   **Compare and contrast the direct measurement of water quality parameters to the use of proxy measures for the overall assessment of water quality in a river.**

4   **Explain the major causes of enhanced (cultural) eutrophication in a river system and describe the measures that may be taken to prevent it occurring.**

5   **Explain how residence time of water in a catchment can influence the water quality response to land use change.**

FURTHER READING

Chapman, D. (ed.) (1996) *Water quality assessments: a guide to the use of biota, sediments and water in environmental monitoring* (2nd edn). Chapman & Hall, London.
A comprehensive guide to water-quality assessment.

Dodds, W.K. (2002) *Freshwater ecology: concepts and environmental applications*. Academic Press, San Diego.
A comprehensive introduction to water quality impacts on the aquatic environment.

Gray, N.F. (1999) *Water technology: an introduction for environmental scientists and engineers*. Arnold, London.
An introduction to the engineering approach for controlling water pollution.