Book Section:

Chapman, PJ, Kay, P, Mitchell, GN et al. (2013) Surface water quality. In: Holden, J, (ed.) Water resources: an integrated approach. Routledge, 79 - 122. ISBN: 0415602823.

Chapter 4

SURFACE WATER QUALITY

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Learning objectives

After reading this chapter you should be able to:

- Understand the natural factors that control surface water chemistry
- Understand how spatial and temporal patterns in surface water chemistry occur
- Explain how water use by humans leads to a deterioration in water quality
- Define the different sources of pollution to surface waters
- Explain how changes in agricultural practices and urbanization affect water quality
- Discuss the causes of acid rain and acid mine drainage, and their impact on water quality
- Understand the role of national and international polices and legislation in reducing water pollution

4.1 Introduction

Surface waters refer to rivers, streams, lakes, ponds and reservoirs. When rain falls on the land it either seeps into the ground to recharge groundwater aquifers (see Chapter 5) or becomes **runoff** which flows downhill over and through the soil into streams, rivers, ponds and lakes (see Chapter 3). However, surface water bodies do not just receive water from runoff, many receive inputs from groundwater (see Figure 4.1), the contribution of which generally increases during periods of low flow. Streams and rivers form where surface water accumulates and flows from land of higher altitude to lower altitude on its journey towards the oceans. Lakes or ponds form where surface runoff accumulates in a flat area, relative to the surrounding land, and the water entering the lake or pond comes in faster than it can escape, either via outflow in a river, seepage to groundwater, or by evaporation. This means that lakes and ponds are standing or very slow moving bodies of water while rivers and streams are distinguished by a fast-moving current. While most lakes contain freshwater, some, especially those where water cannot escape via a river, are salty). In fact, some lakes are saltier than the oceans (see also Chapter 3, section 3.3.2 on closed basins). The terms ‘lakes and ponds’ and ‘rivers and streams’ are often used interchangeably, because in reality there is no obvious distinction between them, although the latter term is typically used when describing a ‘smaller’ standing body of water or running water course, respectively. Reservoirs, also called impoundments, are human-made lakes. However, they can display characteristics of both rivers and lakes because they are created by building a dam across a river and flooding the valley. This damming and flooding creates an artificial lake, filled by the river inflow. Thus the upstream section of the reservoir has predominantly river-like qualities, meaning there is often still some current, while the area closest to the dam is more lake-like.

Stream and river networks drain more than 75 % of the Earth’s land surface. The precipitation that falls on the land percolates over and through vegetation and soil picking up **solutes** (dissolved matter) and sediment along its route to surface waters. Runoff delivers different amounts of solutes and sediment to rivers depending on the **hydrological pathway** it has taken through the catchment and the characteristics of the surrounding landscape (see Figure 4.1). Surface water chemistry is therefore controlled by processes occurring in the river's basin. Thus any changes that occur in the catchment also lead to a change in surface water chemistry. River systems also provide a vital linkage between the terrestrial and aquatic ecosystems. Thus streams and rivers have been referred to as "the environment's circulatory system" (Wetzel, 2001).

This chapter will first consider the natural processes and factors that control the spatial and temporal patterns of surface water chemistry before considering how water use by humans impacts upon water quality. In particular, it will explain how changes in agriculture practices and urbanisation affect water quality and the mitigation factors that are being used to try and reduce water pollution from these sources. This chapter also describes the causes of acid mine drainage, its impact on water quality and mitigation options that exist. The causes of acid rain, its impact on water quality and the how legislation in Europe and North America has lead to the reduction in acid rain are discussed. Finally the chapter will look at the role of national and international polices and legislation in reducing water pollution and how climate change and population growth may affect surface water quality in the future.

4.2 Characteristics of surface waters

It is important to understand the natural processes that control surface water chemistry before exploring the affect of human activities on water quality. The concentration and form of chemical elements and compounds are constantly changing as a result of hydrological, physical, chemical and biological processes. This section briefly discusses the roles of these processes in controlling surface water chemistry.

[Insert Figure 4.1 near here]

Precipitation falling on the land takes a variety of different routes, known as **hydrological pathways**, through the catchment to reach surface waters as shown in Figure 4.1. Precipitation, which has low solute concentrations, may flow downhill over the soil surface, as **infiltration-excess overland flow** (see Chapter 3), or rapidly through the soil via **macropores** to reach rivers and lakes. As the residence time of this water within the catchment is short, the solute concentration of this runoff is usually very similar to that of precipitation. Alternatively precipitation may flow through the soil horizons, where the residence time is longer, before reaching surface waters and solute concentrations increase due to inputs from weathering reactions and microbial activity. Sometimes when the soil is saturated then **saturation-excess overland flow** occurs (see Chapter 3) and this water can be a mix of fresh precipitation and water which has more solutes from within the soil. Lastly precipitation may percolate through the soil into the bedrock below, if it is permeable. At a certain depth below the land surface, called the **water table**, the ground becomes saturated with water, whereas the ground above the water table is unsaturated. If a river cuts into this saturated layer, as shown in Figure 4.1, then water may flow out of the groundwater into the river. This is why even during dry periods there is usually some water flowing in streams and rivers. In addition, due to the longer residence time of this pathway, groundwater tends to be enriched in solutes derived from weathering reactions.

4.2.1 Chemistry

All surface waters contain dissolved (solutes) and suspended (particulate) inorganic and organic substances. The distinction between dissolved and suspended substances is based on filtration, usually through a 0.45 μm membrane filter although other size filters are also used. Particulate matter can impact the **turbidity** (a measure of the amount of suspended particles in the water) which can reduce the light penetration into the water body. High turbidity may impact aquatic life as it reduces the opportunity for **photosynthesis** and impacts animals and plants in the water. Chapter 6 describes such impacts of turbidity changes in more detail. When some compounds (mainly inorganic) dissolve in water they break down (dissociate) to form **ions**, for example, NaCl (sodium chloride) added to water produces Na^+ + Cl^- ions (see Chapter 1). Ions are charged atoms or molecules caused by having an unequal number of protons (positively charged) and electrons (negatively charged); positively and negatively charged ions are normally attracted to each other. Cations are positively charged as they have more protons than electrons. Anions are negatively charged ions. Some elements and ions are very soluble, while others have a strong affinity to stay as particulate matter or become attached to suspended matter.

The major dissolved ions in surface waters, which occur at concentrations exceeding 1 mg L^{-1}, are bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+). In fact these seven ions along with silica (which occurs as $Si(OH)_4$ at the pH of most natural waters) constitute ~95% of the total dissolved inorganic solutes in surface waters. This reflects their relative abundance in the Earth's crust and the fact that they are moderately to very soluble. In contrast, the metals and **metalloids**, which occur at much lower concentrations, are generally found in or bound to the particulate matter in surface waters.

[Insert Figure 4.2 near here]

Some elements exist in a number of different forms while others occur in more than one oxidation state. For example, the most common ionic forms of dissolved inorganic nitrogen in aquatic ecosystems are ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-), while iron can be present as Fe^{2+} (ferrous iron) or Fe^{3+} (ferric iron). The form and oxidation state of an element is mainly controlled by environmental factors, particularly pH and redox potential (see Box 4.1 for definitions of these terms), and has an important control on the solubility and **toxicity** of an element. The influence of pH and redox potential on the oxidation state and hence form of solute in freshwaters is illustrated for iron in Figure 4.2. It can be seen that soluble Fe^{2+} occurs in highly acidic, but well oxidized waters, such as acid mine drainage, and also waters of neutral pH and reducing conditions. However, at neutral pH and oxidizing conditions Fe^{2+} is converted to the insoluble Fe^{3+}, in the form of iron hydroxide ($Fe(OH)_3$). Therefore the iron will precipitate out of solution to become solid matter within the water. This is what occurs when acid mine drainage mixes with surface waters of a higher pH and the iron hydroxide can be observed as a red precipitate on the bed of the river (see Figure 4.13). Other major elements found in surface waters that are strongly influenced by redox reactions are carbon, nitrogen, sulphur and manganese.

Box 4.1

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pH and redox potential

Whether a water body is acidic, neutral or alkaline is determined by measuring the hydrogen ion concentration in solution. In pure water at 24°C, water ionizes (forms ions) to give equal concentrations of hydrogen (H^+) and hydroxide (OH^-) ions: H_2O «» $H^+ + OH^-$. The concentration of both H^+ and OH^- ions is 1×10^{-7} (0.000 000 1) moles per litre. To overcome using these very small concentrations of H^+ ions, a simpler method of using the negative logarithmic of the hydrogen ion concentration was developed, known as pH: $pH = -\log_{10} [H^+]$. Although the pH scale ranges from 1 to 14, with low values the most acidic and high values the most alkaline, most surface waters have a pH range of 4 to 9. As the pH scale is logarithmic it should be remembered that a change of one unit represents a 10-fold change in H^+ ion concentration.

A redox reaction is one where the oxygen state of the substance is changed. For example, a redox reaction occurs when carbon reacts with oxygen to become carbon dioxide. Oxidation involves the increase of oxidation state of a substance (such as in carbon to carbon dioxide) and is associated in a loss of electrons. Reduction is the reverse case. Redox potential (also known as oxidising or reducing potential or Eh) is a measure (in volts) of the tendency of a substance to acquire electrons compared with a standard. The standard used is hydrogen and its redox potential is set to zero:

$$H^{+} + e^{-} \leftrightarrow \frac{1}{2} H_{2(g)}$$

As the redox potential decreases, the solution is more reduced (i.e. has more electrons to give) and as the redox potential increases, the solution is more oxidized (i.e. will accept more electrons).

The sum of all the dissolved solutes plus silica (SiO_2) present in a water body is known as the **total dissolved solids (TDS)**. The TDS can be determined gravimetrically by evaporating a known volume of water and measuring the mass of the residue left. Alternatively it can be determined by the measurement of electrical conductivity as the dissolved ions present in the water create the ability for water to conduct an electric current. When correlated with gravimetric measurements of TDS, conductivity provides an approximation of the TDS concentration of a water sample. However, in very low electrical conductivity waters where the TDS is small such as in some peatland streamwaters, a conductivity meter will not work because an electrical circuit will not be completed. Total dissolved solids in streams and rivers can vary between 50 and 1000 mg L^{-1}, which is at least 20 times the concentration in rain water (Meybeck *et al.,* 1996). In lakes with outlets, TDS are similar to streams and rivers, whereas for lakes without outlets, TDS can range from 1000 to 100 000 mg L^{-1} (Meybeck *et al.,* 1996). Most bottles of mineral water will indicate the value of TDS on their label. Try comparing different brands in relation to the source of the water.

The **Biochemical Oxygen Demand** (BOD) is a commonly measured feature of water quality in surface waters. It equates to the amount of dissolved oxygen (in milligrams) needed by biological organisms in a water body so that they can break down organic matter in a sample of water (normally 1 litre) over a set time period (normally 5 days) for a given temperature (normally 20^{o}C). Typically if there is a lot of organic pollution of a water body the BOD will be very high. Most high quality rivers are thought to have a BOD less than 1 mg L^{-1} while untreated sewage might have a BOD of 50-500 mg L^{-1} (see section 9.3.1 In Chapter 9). If there is a discharge of organic pollutants into a river the oxygen concentration will quickly drop which might result in death of many aquatic animals that need to extract oxygen from the water to survive. This drop of dissolved oxygen concentration after a pollution incident is often known as a sag curve and is shown in Chapter 9 (Figure 9.5). Useful methods for measuring BOD can be found at http://water.epa.gov/type/rsl/monitoring/vms52.cfm.

Another variation of the BOD is the sediment oxygen demand (SOD) which is the usage of dissolved oxygen in the overlying water by sediment chemicals and organisms that live in the sediment on the bed of the water body. Such organisms include burrowing fauna, worms, insect larvae, bacteria, protozoa and fungi. To measure SOD, sediment cores are normally extracted and then oxygen use is measured in the laboratory over a certain period of time at a controlled temperature.

The **Chemical Oxygen Demand** (COD) is another measure of pollution by organic compounds but one which tests the chemical demand for oxygen within the water body without including the biological processing. The COD is a measure of the amount of dissolved oxygen needed to oxidise the organic matter within a litre of water using a standard chemical oxidizing agent. COD is measured in milligrams of oxygen per L of water and is more commonly used in testing wastewater than surface waters in rivers and lakes.

4.2.2 Hydrological processes

Surface water chemistry is strongly influenced by the hydrology of a water body. The residence time of water in streams and rivers usually ranges between two to six months, while that of lakes can vary from months for shallow lakes to 100 years for deep lakes. River and stream flow is unidirectional, usually with good lateral and vertical mixing, but may vary greatly depending on climatic conditions and season. In general, the higher the annual runoff of a river the lower the concentration of solutes, and hence TDS, in a river (Figure 4.3a). This inverse relationship can be explained simply by the dilution of the available solutes as surface runoff volumes increase. However, as the volume of runoff increases so does the total amount of solutes released from the catchment and hence available for transport (Figure 4.3b). This is known as the **solute load** or **flux** and is determined by multiplying the solute concentration by the discharge at a specific location on a river at a certain time. To calculate the annual load of a specific solute, continuous measurements of discharge and concentration are required. However, while discharge can be measured regularly, solute concentration is usually measured less frequently, due to the expense of collecting and analysing water samples. This means that solute concentration must be estimated between sampling periods. Several studies have compared different methods for estimating solute and sediment loads (e.g. Littlewood, 1992; Webb *et al.*, 1997) and have found that regular monitoring programmes tend to over-emphasise base flow components which is compounded the longer the time interval between samples. Webb *et al.* (1997) investigated the effect of different methods to estimate chemical fluxes for the River Derwent in Yorkshire, UK, and found that for 20 out of the 36 determinands investigated, the difference between the minimum and maximum load estimate, expressed as a percentage of the minimum value, exceeded 50%, and for five determinands, the difference was greater than a 100%.

[Insert Figure 4.3 near here]

In catchment studies, the annual dissolved load serves as an integrated measure of all the processes that occur within the river basin that affect stream water chemistry. While measurement of solute concentration informs us how much of a particular solute is present at a specific point in time and is useful for comparing with water quality standards, solute loads can be used to quantify the amount of solute entering a specific water body, such as a lake or ocean, from terrestrial sources or the impact of environmental changes on the terrestrial cycle of nutrients. In order to compare solute loads from catchments of different size the load is divided by the area of the catchment and is generally expressed in tonnes per km^2 per year (which is equivalent to g m^{-2} yr^{-1}) (see Box 4.2).

Box 4.2

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Calculating solute loads for Eagle Creek, Indiana

Table 4.1 shows some example data for stream discharge and nitrate concentrations at hourly intervals for Eagle Creek at Zionsville in Indiana which were obtained from the USGS database which is a public domain source. Data are for one day in January 2013. The drainage area is 274.5 km^2. We would like to determine the total flux of nitrate from the catchment and, so we can fairly compare it to data from other sites, to calculate the solute load for the day per unit catchment area.

Table 4.1 Nitrate-N concentrations and discharge for a 24 hour period 2-3 January 2013 for Eagle Creek, at Zionsville, Indiana.

Time	**Discharge m^3 s^{-1}**	**Nitrate-N, mg L^{-1}**
18:00	2.18	3.22
19:00	2.15	3.31
20:00	2.10	3.34
21:00	2.18	3.39
22:00	2.35	3.36
23:00	2.29	3.39
00:00	2.29	3.39
01:00	2.35	3.40
02:00	2.38	3.36
03:00	2.55	3.37
04:00	2.55	3.40
05:00	2.61	3.42
06:00	2.61	3.45
07:00	2.69	3.45

08:00	2.80	3.48
09:00	2.97	3.40
10:00	3.14	3.45
11:00	3.37	3.47
12:00	3.60	3.40
13:00	3.09	3.36
14:00	2.61	3.37
15:00	2.10	3.45
16:00	1.95	3.50
17:00	2.01	3.60

Multiplying the discharge value for each hour by the number of seconds in each hour gives us an estimate of total discharge in that hour in m^3. In order to put everything in the same units we can divide the concentration of nitrate by 1000 to express it as mg per m^3 of water (since there are 1000 litres in a m^3). If we then assume that the concentration of nitrate applies for the whole hour then multiplying that concentration by the total discharge for the hour we end up with a value of mg of nitrate that has moved passed the gauging point on the river. Taking the first row of data from Table 4.1 as an example gives us 7849.4 m^3 of water for that hour (multiply 2.18 m^3 s^{-1} by 3600 s). If we multiply 0.0032 mg m^{-3} of nitrate by 7849.4 m^3 of water we obtain a total flux for the hour of 25.3 mg of nitrate. Repeating this for each hour and summing the total provides us with an estimate of 747 mg of nitrate for the 24 hour period shown in the table. As the catchment area is 274.5 km^2 we can suggest that for one 24 hour period the nitrate flux from Eagle Creek was equivalent to 2.7 mg km^{-2}. This is a very low value (equivalent to under 1 g km^{-2} yr-1, but the sampling occurred in a cold winter month when there is some frozen ground and we only used one day as an example. Obviously we could repeat this for the whole year quite easily in a spreadsheet to provide a more realistic annual flux estimate.

In many cases we do not have data at such high frequency as presented above. While we might have good discharge data collected at high frequency (e.g. every 15 minutes) often water quality samples for different solutes are taken once per week or sometimes less frequently, occasionally supplemented by sampling during some storm events. In these instances it is not suitable simply to multiply discharge at the time of sampling by concentration of the solute and then sum the values. That is because we do not have values of concentration for all of the times in between (when the discharge and concentrations might be quite different). Therefore we need to interpolate values between sample points to produce a value of annual solute load. The methods most commonly used vary depending on what data is available and are described in Walling and Webb (1985).

Lakes and reservoirs are characterised by alternating periods of **stratification** and vertical mixing which has an effect on water chemistry. Stratification in lakes or reservoirs occurs when the water acts as two different bodies with different densities, one floating on the other. It is most commonly caused by temperature differences within the water column, particularly in deep (> 10 m) temperate lakes and reservoirs because of seasonal changes in temperature. It is less common in tropical lakes where temperature varies little over the year. Stratification results in different processes dominating in the different layers of the lake. In temperate regions during the summer, the surface layer, known as the **epilimnion**, receives more sunlight, is warmer and has an oxidizing environment because it is exposed to the atmosphere. In contrast, the deeper layer, known as the **hypolimnion** is separated from the epilimnion by a **thermocline** (see Chapter 6). Due to the isolation of the hypolimnion from the atmosphere, it is cooler and receives less oxygen leading to anoxic conditions developing in the lake bottom sediments. This gradient of dissolved oxygen means that elements that have more than one oxidation state occur in the oxidised state in the epilimnion and the reduced form in the hypolimnion (Figure 4.4). Thus stratification of reservoirs can lead to concentrations of iron and manganese exceeding drinking water quality standards. This is because the reduced forms of these metals are much more soluble than the oxidised forms. Therefore the metals within the sediments on the reservoir bottom will leach out and dissolve in the water and if water is abstracted from the hypolimnion in the reservoir then high concentrations of dissolved lead and manganese will be found in the abstracted water.

[Insert Figure 4.4 near here]

Reflective question

What is a redox reaction?

4.3 Spatial variation in surface water chemistry

In natural conditions, the chemistry of surface waters is controlled by three main processes (Gibbs, 1970; Meybeck *et al.*, 1996; Walling and Webb, 1986): (i) atmospheric inputs, (ii) weathering of bedrock and (iii) climate (evaporation-crystallisation processes). The main source of atmospheric inputs is from oceanic aerosols (Na and Cl), however other sources include volcanic emissions (such as SO_2), and dissolution of soil-derived particulates (such as Ca, HCO_3 and SO_4). The distance from the ocean will determine the extent to which sea-spray rich in Na, Cl, Mg and SO_4 influences surface water chemistry. In coastal areas, where oceanic inputs may dominate over all other sources, Na and Cl are the most abundant solutes in surface waters. These solutes may also dominate in areas where rocks are extremely resistant to weathering, such as in central Amazon.

In nearly all major rivers of the world, calcium is the dominate cation and bicarbonate the major anion. In fact, 80% of the dissolved load of the major rivers of the world is made up of just four solutes; calcium, bicarbonate, sulphate and silica (Walling and Webb, 1986). The major source of these solutes is the weathering of bedrock. The susceptibility of rocks to weathering varies from low for **plutonic** and **metamorphic** crystalline rocks to high for sedimentary rocks such as limestone and chalk. Thus TDS in rivers and streams draining catchments underlain by sedimentary rocks are five times greater than in rivers draining catchments dominated by crystalline rocks and about two and a half times greater than catchments underlain by volcanic rocks (Meybeck, 1981). In some areas of the world, where rock type is very homogeneous, such as the Canadian and African shields and the Amazon and Congo basins, stream water chemistry may vary very little over large areas. In contrast, stream water chemistry can be highly variable in areas where geology varies on the finer scale. Overall, approximately 60 % of all the solutes present in surface waters are derived from the weathering of rocks (Walling and Webb, 1986).

The influence of climate on surface water chemistry is very important at the global scale. As well as controlling the rate of weathering, through its influence on temperature and water availability, climate controls the water balance. In areas where evaporation exceeds precipitation, solutes derived from both weathering and atmospheric inputs are gradually concentrated. If evaporation is high enough, some minerals will start to precipitate, such as calcite ($CaCO_3$) and dolomite ($MgCO_3$). The precipitation of minerals results in the surface waters containing lower concentrations of Ca and HCO_3 and higher concentrations of Na, Cl, Mg and SO_4. In contrast, in areas where annual rainfall is high, the concentration of solutes in surface waters is diluted.

It has been proposed that because the above three processes influence the concentration of the major solutes in different ways, the relative abundance of the dominant cation and anion can be used to evaluate which of the processes is most significant in controlling surface water chemistry (Figure 4.5). High concentrations of Na and Cl, with low TDS, are observed in wet coastal regions where atmospheric inputs are the dominant source of solutes and inputs derived from weathering are low. Sodium and Cl can also dominate in semi-arid areas where evaporation-crystallization processes dominate resulting in very high TDS. However, Gibb (1970) found that most surface waters were dominated by Ca and HCO_3 derived from the weathering of bedrock and plot in the central region of Figure 4.5. This was supported by the findings of Meybeck (1981) in his survey of global rivers (representing about 60 % of the water discharge to the oceans), where he observed that 97 % of rivers were dominated by Ca and bicarbonate and that Na was the dominant cation in only 1.7 % of rivers and Cl and SO_4 were dominant in just over 1 % of rivers. Thus the classification of Gibbs (1970), although attractive in its simplicity, is of limited value. In addition, other surface waters deviate from the plot in Figure 4.5, due to extreme geological or climatic conditions. For example, very acidic waters are often found in active volcanic regions or in sedimentary rocks rich in metal sulphides.

[Insert Figure 4.5 near here]

Reflective question

Are TDS in surface waters likely to be greater or smaller in warmer, drier climates than elsewhere?

4.4 Temporal variations in surface water chemistry

Surface water chemistry varies over time for two main reasons. Firstly the processes controlling the supply of solutes available for leaching vary over time and secondly the hydrological processes that generate runoff within a catchment are dynamic and vary with climate and season. The major temporal patterns in surface waters can be considered at the following timescales:

1. During storms (hours) as a result of changes in hydrological flowpaths delivering different sources and amounts of solutes.
2. Diurnal (24-hour) variations in for example pH and dissolved oxygen, resulting from biological processes and changes in daylight.
3. Seasonal variations associated with biological and hydrological cycles.
4. Year to year trends, usually as a result of anthropogenic activities in the catchment.

Fluctuations in dissolved oxygen concentration and pH are primarily related to photosynthesis and aerobic respiration of aquatic plants. Photosynthesis, which is driven by sunlight, removes carbon dioxide (CO_2) from the water and produces free oxygen, which causes an increase in surface water pH and dissolved oxygen. However, stream water pH and dissolved oxygen concentrations are also affected by changes in air pressure and temperature. The solubility of gases increases as air pressure increases; this can influence the pH of water, as more CO_2 will dissolve in the water as air pressure rises. In contract, increases in temperature reduce the solubility of most gases; cold water can hold more dissolved oxygen than warm water. Therefore the dissolved oxygen content of surface water has both a seasonal and diurnal cycle, as shown in Figure 4.6. This diurnal variation in dissolved oxygen is not generally observed from collecting regular water samples as this typically occurs in the daytime. However, the use of continuous monitoring probes has enabled these small diurnal variations to be clearly observed (Figure 4.6).

[Insert Figure 4.6 near here]

During storms, changes in dominant hydrological flowpaths though the catchment (Chapter 3) can lead to large changes in solute concentrations, over relatively short periods of time. For some solutes, an increase in river discharge can lead to an increase in concentration as solutes are moved rapidly into the river by overland flow and shallow throughflow. For example, dissolved organic carbon (DOC) concentrations can increase with stream discharge during storms in some catchments (Chapman *et al.*, 1993; Hinton *et al.,* 1992; Figure 4.7a). This reflects the change in hydrological flowpaths with more flow through the upper organic surface soil horizon in the catchment where DOC is produced. In contrast, other solutes that are mainly derived from the weathering of bedrock, such as Ca and Mg, and transported to surface waters by deep soil throughflow and groundwater display a negative relationship with discharge during storms (Figure 4.7b) as their concentrations are diluted by surface runoff.

[Insert Figure 4.7 near here]

Many solutes display strong seasonal patterns (Figure 4.8). These patterns can be divided into those that are controlled by seasonal changes in hydrology and those that are mediated by biological processes. In streams and rivers, pH and concentrations of Ca and Mg often display a maximum in summer and minimum in winter, which reflects seasonal changes in the dominant source of water (Figure 4.8a). In summer, groundwater enriched in base cations often dominates stream flow, whereas in winter soil water and surface runoff, that is more acidic and contains lower concentrations of base cations, dominates. In natural waters, nitrate (NO_3) and potassium (K) also display strong seasonal patterns with a summer minima and winter maxima (Figure 4.8b). This reflects seasonal changes in the availability of these nutrients for leaching as plant uptake during the summer reduces the concentration of these nutrients in soil solution. Dissolved organic carbon (DOC) is also strongly mediated by biological processes; being produced via the decomposition of organic matter during summer and washed from the soil during the autumn. Hence DOC displays a maximum in late summer and autumn and a minimum in early spring (Figure 4.8c).

[Insert Figure 4.8 near here]

Long-term patterns in surface water chemistry are usually driven by climatic variability, and anthropogenic activities, such as changes in land management or atmospheric pollution. However, it is often difficult to identify the main driver of change as many of these factors are changing at the same time or the record of solute concentration (often referred to as a time-series) is of insufficient length. A number of studies have highlighted that caution is needed in interpretation of 'long-term' river and lake water chemistry and that misleading conclusions may be drawn from data sets of 10 years or less (e.g. Burt *et al.*,1988; Driscoll *et al.*, 1989). For example, analysis of stream water NO_3 concentrations from the Hubbard Brook Experimental catchment, northeast United States, for the period 1964-1974 suggested a strong increasing trend (Liken *et al.*, 1977). However, no long-term trend was observed in the data set for the period 1964-1987 (Driscoll *et al.*, 1989). This illustrates the importance of maintaining long-term sites and networks of surface water chemistry.

Long-term records of surface water NO_3 concentrations for semi-natural catchments generally show no evidence of time trends, despite an increase in atmospheric nitrogen deposition at many of these sites caused by air pollution. However, peak winter concentrations do vary markedly between years (e.g. Reynolds *et al.,* 1992; Mitchell *et al.*, 1996). This variability has been explained by inter-annual variation in climatic factors, including drought, summer temperature and winter freeze-thaw. For upland lakes and streams across the UK, Monteith *et al.* (2000) observed that the mean December-March **North Atlantic Oscillation (NAO) index** (a measure of large scale climate conditions a bit like the El Nino Southern Oscillation) was a good indicator of peak NO_3 concentration. Highest peak NO_3 concentrations were observed when the NAO values were lowest, which indicates drier, colder weather in north-west Europe. Therefore, Monteith *et al.* (2000) suggested that freezing of the soil leads to the death of some of the soil microbial biomass and damage to plant roots and subsequent thawing leads to the release of this material available for mineralization and leaching to surface waters.

In the 1980s and 1990s, many countries set up atmospheric and stream or lake monitoring networks to determine the impact of emission controls implemented at coal fired power stations on improving air and water quality. Although atmospheric SO_4 deposition has declined rapidly across North America and Europe over the last 20 years (e.g. Jeffries *et al.,* 2003; Forsius *et al.,* 2003; Fowler *et al.,* 2005) surface water acidification remains an issue, despite many studies observing a decline in stream water SO_4 concentrations (Stoddard *et al.,* 1999; Davis *et al,* 2005; Skjelkvale *et al*., 2005; Burns *et al*., 2006; Figure 4.9). This lag in surface water acidification recovery has been attributed to a range of processes, including deposition of N remaining high, depletion of base cations and increase in dissolved organic carbon (DOC) concentrations. This demonstrates the long-term influence of biogeochemical processes occurring within a catchment on surface water chemistry.

[Insert Figure 4.9 near here]

<u>Reflective question</u>

Ignoring human influence, what are the key reasons that solute concentrations naturally vary over time in surface waters?

4.5 Water use and water quality deterioration

Although surface freshwater which is not locked up in ice sheets, glaciers or permafrost only accounts for less than 1 % of all the non-saline water on Earth, it is essential for the survival of terrestrial life and without it humans could not survive. In addition to providing drinking water, humans use water for a wide variety of purposes that both consume and contaminate the water. Since ancient times, surface waters have been used as a convenient disposal route for our waste. However, this use (or abuse) of surface waters for waste disposal conflicts with almost all others uses of water and most seriously with the use of surface waters for drinking water (see Chapter 9).

The industrialisation of a country leads to a shift in the pattern of water use from rural and agricultural to urban and industrial and the growth of large cities has been accompanied by increasing stress on the aquatic environment leading to a reduction in the quality of the water (McDonald *et al.*, 2011 and see section 4.6.2 on urbanisation). Poorer water quality means water pollution.

Water pollution is usually defined as 'where one or more substances have built up in a water body to such an extent that it can be harmful to organisms and plants which live in the water body and to animals and humans that may drink the water'. Although water pollution usually refers to a deterioration in water quality caused by human activities, the same effect may occur naturally. For example, large amounts of sediment can be washed into streams and rivers during rainstorms and toxic metals find their way into surface waters where concentrations of metal ores occur. These are natural processes and the environment will be able to neutralise affects on water quality with time. Pollution caused by human activities, on the other hand, are usually on a larger scale, can often happen rapidly and can take a much wider variety of forms as outlined in Table 4.2.

Table 4.2 The nature, sources, effects and control of some major types of pollutants.

Pollutant	Nature	Source	Effects	Control
Bacteria	Disease causing organisms	Domestic sewage and animal waste	Illness to humans and curtailed recreation use	Treatment of waste (e.g. at sewage treatment works) and chlorination of drinking water
Nutrients	Mainly refers to nitrogen and phosphorous species	Domestic sewage, industrial waste and agricultural land (mainly inorganic fertiliser)	Excessive growth of aquatic plants leading to eutrophication; high nitrate concentrations in drinking water potentially toxic	Phosphorus removed at sewage treatment works. Reduce nitrate leaching by controlling fertiliser inputs and good land management
Trace metals		Mining, industrial processes, runoff from roads	Toxic effects on aquatic ecosystems	Difficult

Organic chemicals	Pesticides, detergents, industrial by-products and pharmaceutics.	Domestic sewage, industrial waste and farms	Toxic – threat to fish and other aquatic fauna; possible impacts on human health	Difficult to control as not removed by conventional sewage or water treatment works
Natural organic matter	Biodegradable organic material decomposed by aerobic bacteria (requires dissolved oxygen)	Domestic sewage, animal manure, food-processing	Causes depletion in dissolved oxygen content that has an impact on aquatic fauna and flora.	Treatment of sewage, containment of sewage, animal slurry and manure and silage effluent.
Sediment	Mainly soil material (organic & inorganic); industrial by-products	Land erosion by water and wind, construction sites, some quarrying and mining processes	Removal of fertile soil, filling of reservoirs and lakes, sedimentation of gravel beds; reduced aquatic life	Controlled by soil conservation and best management practices; use of settling ponds; flood control
Heat	Heated water returned to rivers and lakes	Power stations, steel mills and refineries and other industrial cooling units.	Reduces dissolved oxygen content of water and potential harm to aquatic life.	Minimised by recirculation and reuse of industrial cooling waters.

Pollution sources that affect surface water are usually separated into two categories:

(i) Point sources

(ii) Non-point sources or diffuse pollution.

If pollution comes from a single location, such as a discharge pipe attached to a factory, it is known as **point-source pollution**. Other point sources include sewage treatment plants, industrial discharges, or any other type of discharge from a specific location (commonly a pipe) into a stream. By contrast, **non-point sources** are **diffuse sources** of pollutants that are not as easily identified or measured as point sources. Common examples include:

- Excess fertilizers and pesticides from agricultural and residential lands
- Sediment from agricultural and forest lands, construction sites, and eroding stream and river banks
- Bacteria and nutrients from livestock wastes and leaking septic tank systems
- Salt, oil, grease and heavy metals from urban runoff
- Acid drainage from abandoned mines
- Atmospheric deposition

When point-source pollution enters the aquatic environment, the place most affected is usually the area immediately around the source. However, it is also dependent on the capacity of the receiving water body to dilute the input and the ecological sensitivity of the receiving water. In contrast, the location most affected by diffuse pollution may be far downstream from the location where the pollutant entered the watercourse as it is often the cumulative effect of small amounts of contaminants gathered from a large area that results in an impact. Where pollution enters the environment in one place but has an effect hundreds or even thousands of miles away, this is known as **transboundary pollution**. An example of this is the emission of pollutants, such as sulphur dioxide (SO_2), into the atmosphere in one country which is then deposited in another country having an impact on water quality (see section 4.6.4 on acid rain).

Different sources of pollution respond to storms in contrasting ways. Usually, the concentration of pollutants from non-point sources will increase as flow increases during storm runoff. In contrast, concentrations of pollutants from point sources generally decrease through dilution during storm runoff. Thus water monitoring programmes that collect water samples at regular time intervals (usually weekly or monthly) are much more likely to identify point sources of pollution which can be treated. In contrast, pollution from diffuse sources can only be controlled by prevention and remain the major challenge to improving surface water quality globally.

There are two main ways of measuring the quality of water. One is to take water samples and measure the concentrations of different solutes and sediments that it contains. If the concentrations exceed a certain limit, we can regard the water as polluted. Measurements like this are known as chemical indicators of water quality. An alternative method is to examine the fish, insects, and other invertebrates that live in the aquatic environment. A widely used system focuses on macroinvertebrate benthic fauna and utilises the Biological Monitoring Working Party (BMWP) scoring system (Armitage *et al.*, 1983) to assess water quality. Measurements like this are called biological indicators of water quality. Often both types of measurements are made to classify the quality of a water body. For example, the European Water Framework Directive (WFD) requires member states to use chemical and biological indicators, along with hydrogeomorphological parameters, to rank the ecological status of rivers (see Box 6.3 in Chapter 6).

Reflective question

Why might the people responsible for diffuse pollution often be difficult to trace?

4.6 Surface water pollution: causes, consequences and management

4.6.1 Agriculture

Farm type can be split generally into arable and livestock. Common arable crops include wheat, barley, rice, oats and oil seed rape, as well as vegetables, such as potatoes and other root crops. Livestock farms tend to focus on one particular type of production, which might be dairy, beef, sheep or pigs. Some of these farms will operate intensive indoor systems whilst others will use more extensive outdoor production techniques.

4.6.1.1 Impacts of agriculture on water quality

Agriculture can have a huge impact on water quality due to the vast array of chemicals that are used to increase production. It is thought that the aquatic life in the Gulf of Mexico is severely degraded by agricultural pollution brought down the Mississippi river from the heavily agricultural mid-west of the USA. The USGS estimates that 70 % of the nitrogen and phosphorus that enters the Gulf of Mexico comes from agricultural sources in the USA. This compares to 9-12 % from urban sources. Nutrients are one of the most well studied agricultural pollutants and comprise largely of nitrogen and phosphorus which are applied to land in manure and slurry (Figure 4.10) as well as in inorganic fertiliser. Moreover, dung is deposited on fields by grazing livestock. Nitrate is the major form of nitrogen found in surface waters and is very mobile, unlike some other forms, such as ammonium, which is more strongly retained by soils (Hatch *et al.,* 2002). Nitrate leaching is a problem in most agricultural areas and peak concentrations in rivers usually exceed 10 mg N L^{-1}, although the other nitrogen species will be found at much lower concentrations (Neal *et al*., 2006). Although not particularly toxic in the environment, nitrate must be removed from drinking waters which is costly to water utilities and consumers (Pretty *et al*., 2000). In contrast, phosphate tends to form **complexes** with soil particles and concentrations in rivers are, thus, often associated with levels of suspended solids. Nevertheless, orthophosphate is soluble and is therefore **bioavailable** to aquatic organisms, which can lead to **eutrophication** (an unwelcome bloom of plants in water which has a detrimental effect on other organisms) as plants can quickly use the phosphate to encourage rapid growth (Jarvie *et al.,* 2007).

[Insert Figure 4.10 near here]

Pesticides, including herbicides, insecticides and fungicides, are applied to a wide variety of crops in order to improve growth by eliminating competitors and parasites. Residues of these chemicals are frequently transported from crops and soils to waters in runoff (Garrod *et al*., 2007). The extent to which these substances are present in waters will depend largely on their physicochemical properties, which determine their degradation and **sorption** (how one substance becomes attached to another) characteristics (Kladivko *et al*., 1991). The degradation rate of a pesticide is usually expressed as its half-life (DT_{50}) (i.e. the time taken for the substance to degrade to 50 % of its original concentration). Sorption characteristics are expressed as values representing the amount (per kg) of a substance that will attach to soil (abbreviated to K_d). As for phosphorus though, sorption of a pesticide to soil does not mean that it will be immobile as substances can be transported in the particulate phase in overland flow and subsurface drainflow (Øygarden *et al.,* 1997). Concentrations of pesticides detected in water bodies range from nanograms per litre, ng L^{-1}, (billionths of a gram) up to tens of micrograms per litre, $\mu g\ L^{-1}$ (millionths of a gram), although they are commonly measured in streams at peak concentrations below 10 $\mu g\ L^{-1}$, (Du Preez *et al.,* 2005).

Veterinary medicines have similar physicochemical properties to pesticides but reach the land following administration to livestock to prevent and treat disease. Residues of these compounds can be found in manure and slurry applied to land and in dung deposited by grazing livestock. Moreover, wash-off can occur following topical application. Antibiotics are the most commonly used group of veterinary medicines and have been measured in rivers at concentrations up to a few $\mu g\ L^{-1}$. Toxic impacts are unusual in the aquatic environment although concern exists about the spread of antibiotic resistance (Kay *et al.,* 2004).
Other important water quality issues resulting from agricultural production include sediment loss (Edwards and Withers, 2008) and organic pollution from manures and silage effluent leading to significant reductions in the dissolved oxygen content of water bodies (Hooda *et al.*, 2000).

4.6.1.2 Agricultural stewardship

Due to the known impacts that agriculture can have on the environment, the implementation of stewardship measures is now common place and many of the subsidies available to farmers today are offered on this basis rather than being related to production. Specific measures have long been proposed to reduce the impacts of agriculture on water quality. Stewardship measures can be split into three general categories; those that reduce inputs of pollutants; others that limit transport to waterbodies; and edge of field measures (Kay *et al.*, 2009). Hundreds of measures are available that can be implemented by farmers but some of the most common include **buffer zones**, wetlands and specific soil management practices. Buffer zones involve creating areas of land near waterbodies that are not used for farming. These buffers use a protected strip of vegetation (perhaps 8-50 m wide) to trap and consume pollutants, including sediment, before they enter watercourses. The use of buffer zones has been found to be very successful in reducing pollution of water bodies, but farmers have to accept that valuable land is taken out of production in such schemes. There are many examples of agricultural stewardship schemes around the world, including work undertaken by the Environmental Protection Agency in the US and the Landcare scheme in Australia. Furthermore, many stewardship measures have been implemented in the UK through the England Catchment Sensitive Farming Delivery Initiative (ECSFDI) in recent years (Figure 4.11). This is a scheme set up to encourage farmers to adopt environmentally friendly practices through programmes of advice and the availability of subsidies paid through Cross Compliance and the Entry and Higher Level Schemes.

[Insert Figure 4.11 near here]

4.6.1.3 The future

There are a number of contemporary issues that are particularly pertinent as to future impacts of agriculture on water quality. Whilst stewardship measures have been implemented for a number of years and with renewed vigour since reform of the European Common Agricultural Policy in 2003 there is a limited amount of data to support their use to improve water quality (Box 4.3). Whilst great impacts have been made in some cases these are likely to be site and pollutant specific and for many measures no data are available. Crucially, limited data exist to describe the impact of stewardship at the catchment scale (Kay *et al.,* 2009).

Furthermore, subsidies for agricultural stewardship may change in the future with little certainty that current regimes will remain. It has been postulated that human population growth will require agricultural production to be increased and therefore subsidies for environmental protection could be replaced once more by production related payments.
At present, agriculture remains one of the key sources of surface water pollution and there is currently little evidence to suggest that this situation is improving, despite concerted efforts to employ more environmentally friendly practices.

BOX 4.3

CONTEMPORARY CHALLENGES

Long-term nitrate trends in rivers

The use of fertilisers in agriculture has helped to ensure the production of plentiful, cheap food supplies in the developed world, although one of the consequences of this has been nitrate pollution of rivers. Subsequently, policies have been developed that have attempted to reduce this contamination; including the EU Nitrates Directive (EC, 1991) and the Clean Water Act in the US (US Senate, 2002), which have set regulatory limits for nitrate concentrations in rivers of 11.3 and 10 mg N L^{-1}, respectively. Recent studies to assess how effective these policies have been have determined that nitrate concentrations in polluted rivers have generally changed little in recent decades (since the 1970s) (Worrall *et al.,* 2009; Burt *et al.,* 2011; Kay *et al*., 2012; Figure 4.12). In the Mississippi basin, for example, despite efforts to reduce pollution, nitrate losses to the Gulf of Mexico were actually 10 % higher in 2008 than they were in 1980 (Sprague *et al.,* 2011). This has been attributed to increased concentrations at upstream sites which, when normalised for changes in flow, have risen by around 75 %. A particular problem is that nitrate can take decades to reach groundwater and then be transported to streams and so the impacts of land management actions may not be evident for many years. Moreover, some work has highlighted that it may not be the inherent ability of some agricultural stewardship measures (e.g. reduced fertiliser applications) to reduce nitrate pollution that is the problem but rather the need for robust implementation of these by regulators and farmers (Kay *et al*., 2012). Taking these factors into account, it may not be possible to achieve some policy goals, such as compliance with the EU Water Framework Directive by 2015. If progress is to be made though, continued efforts will be needed on farms to control nitrogen inputs and transport to waters, as will long-term (covering several decades) water quality data sets to assess their impacts.

[Insert Figure 4.12 in here]

4.6.2 Urbanization

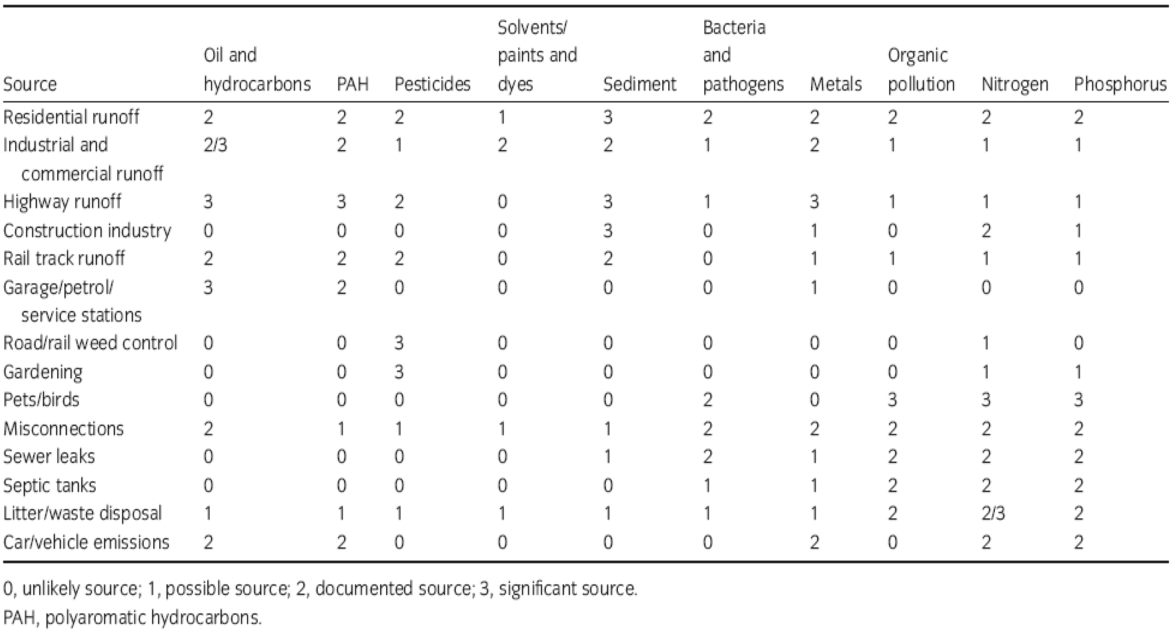
4.6.2.1 Urban pollution and non-point sources

Many towns and cities develop in close proximity to lakes and rivers. The construction of housing, commercial buildings, roads and other infrastructure, reduces the permeability of the surrounding land, and so alters the hydrological characteristics of stormwater flowing to those lakes and rivers. Runoff volumes increase and most obviously discharges become ‘flashy’, with a shorter time to a greater peak discharge, resulting in increased bed and bank scour and increased risk of flooding. Loss of in stream and riparian biodiversity also occurs, exacerbated by the low or zero flows that can then occur during dry weather. Such urbanisation also has major impacts on water quality. Historically, impacts of most concern were those associated with sewage disposal and end-of-pipe (e.g. factory) discharges. Investment in sewers and wastewater treatment processes, driven by public health imperatives (see Chapter 9), and greater regulation of commercial point source discharges have led to dramatic improvements in the quality of urban surface waters in many countries over the last 150 years. However, urban waters often remain unacceptably polluted, due to emissions from non-point sources which originate over an area. These emissions comprise a diverse mix of pollutants that accumulate on built surfaces, until they are washed off during storm events (see Box 4.4 for an example). Impacts may then arise due to sedimentation of rivers (e.g. light loss, gill rot in fish), dissolved oxygen depletion, eutrophication, transmission of infectious pathogens, and a wide range of toxic effects from metals, biocides and other persistent organic pollutants.

Table 4.3 indicates the range of urban pollutants involved, and their principal sources. While most pesticide pollution is associated with agriculture, some pesticides are often used in gardens in urban areas which can be problematic (e.g. metaldehyde products are used to kill slugs). Table 4.4 reveals that the concentration of many of these pollutants in urban stormwater exceeds that of untreated sewage or from combined sewage overflows (CSOs) which comprise a mix of untreated sewage and storm water, discharged to river when storm discharges would otherwise exceed sewer capacities. Data limitations mean that it is difficult to understand precisely the role of urban diffuse sources in river degradation, but evidence (see for example Table 4.5), suggests that in developed countries urban diffuse pollution is now one of the main reasons that rivers fail to reach their water quality objectives. Note that when CSOs are also considered, urban storm water pollution accounts for more kilometres of poor water quality than any other cause.

It should also be noted that many possible urban water pollutants are not yet being monitored as the detection techniques are only just becoming available. These pollutants include those derived from pharmaceuticals and personal care products such as steroids, antibiotics, fire retardants, fragrances and flavours, insect repellents, disinfectants, cosmetics, solvents, hair dyes and so on. In many cases it is not known what effects many of these substances might have on aquatic organisms or human health and this is an emerging area of study for water science. However, it is known that many synthetic chemicals act as endocrine disrupters in the aquatic environment. This means they can cause the sex of some creatures to be altered at the foetal stage. Much further research is required on a wide range of these urban pollutants.

Table 4.3 Some urban diffuse pollutants and their sources (from Ellis and Mitchell, 2006). Reproduced with kind permission of John Wiley & Sons from Ellis, J.B. and Mitchell, G. 2006. Urban diffuse pollution: key management issues for the Water Framework Directive. *Journal of the Chartered Institution of Water and Environmental Management* 20: 19-26.



Source	Oil and hydrocarbons	PAH	Pesticides	Solvents/ paints and dyes	Sediment	Bacteria and pathogens	Metals	Organic pollution	Nitrogen	Phosphorus
Residential runoff	2	2	2	1	3	2	2	2	2	2
Industrial and commercial runoff	2/3	2	1	2	2	1	2	1	1	1
Highway runoff	3	3	2	0	3	1	3	1	1	1
Construction industry	0	0	0	0	3	0	1	0	2	1
Rail track runoff	2	2	2	0	2	0	1	1	1	1
Garage/petrol/ service stations	3	2	0	0	0	0	1	0	0	0
Road/rail weed control	0	0	3	0	0	0	0	0	1	0
Gardening	0	0	3	0	0	0	0	0	1	1
Pets/birds	0	0	0	0	0	2	0	3	3	3
Misconnections	2	1	1	1	1	2	2	2	2	2
Sewer leaks	0	0	0	0	1	2	1	2	2	2
Septic tanks	0	0	0	0	0	1	1	2	2	2
Litter/waste disposal	1	1	1	1	1	1	1	2	2/3	2
Car/vehicle emissions	2	2	0	0	0	0	2	0	2	2

0, unlikely source; 1, possible source; 2, documented source; 3, significant source.
PAH, polyaromatic hydrocarbons.

Table 4.4 Pollutant concentrations in wastewater and storm water across Europe (data from Mitchell, 2001; Novotny, 2002 and Rule *et al*., 2006b)

	Untreated sewage	CSO	Urban stormwater
BOD mg L^{-1}	160	60-200	10-250
SS mg L^{-1}	225	100-1100	3000-11000
Total N mg L^{-1}	35	3-24	3-10
Total P mg L^{-1}	10	1-11	0.2-1.7
Coliforms MPN/100mL	10^7-10^9	10^5-10^7	10^3-10^8
Cadmium μg L^{-1}	0.15-0.38	1.4-9.6	0.2-63
Copper μg L^{-1}	110-240	80-170	2-1270

Zinc µg L^{-1}	85-180	100-1070	17-3550

Table 4.5 Causes of low river quality in Scotland (data from SEPA, 1996)

Cause	**% of river length**
Abandoned mines	22
Sewage from treatment works	21
Urban diffuse sources	20
Combined sewer overflows (CSOs)	12
Industry	12
Agricultural point sources	4
Agricultural diffuse sources	1
Other	8

Box 4.4

CONTEMPORARY CHALLENGES

De-icing agents and diffuse pollution

In cold regions, highway authorities often undertake preventative measures to avoid road icing in winter. Salt is the most common de-icing agent and typically comprises about 90% sodium chloride, with the remainder made up of insoluble residues such as clay marl, and trace amounts of metals. Colwill *et al.* (1984), estimated that de-icing contributed 25 % of suspended loadings and 90 % of soluble loadings in winter road runoff from a rural motorway in England, although clearly this will vary greatly with frequency and extent of salt application. The chloride contained in road salt is a concern due to its impact on ground and surface waters used for drinking supply and aquatic habitat. The metals contained in de-icer salt, including nickel, lead, zinc, and chromium are toxic in runoff, whilst the salt itself increases the solubility and mobility of metals previously deposited on road surfaces by vehicles. De-icer salt also contains sodium ferrocyanide, added as an anti-caking agent, which in strong sunlight and acidic conditions can generate toxic cyanide forms, although in surface waters this usually evaporates as hydrogen cyanide.

Monitoring in northeastern USA from 1991-2004 indicated chloride concentrations exceeded environmental standards in around 2 % of the 1300 groundwater wells analyzed, whilst 15 of 100 catchments had winter chloride concentration in excess of aquatic habitat standards (Mullaney *et al*., 2009). Concentrations were greatest in urban areas, where available data indicated an increasing historical trend in chloride loading. For the urban areas, chloride: bromide ratio analysis indicated that much of the chloride was due to de-icer application, although septic systems, wastewater discharge, and saline groundwater plumes from landfills and salt-storage areas were also significant sources. The increasing load in chloride, consistent with literature reports of long term increases in chloride concentrations, was attributed to the expansion of road networks and impervious areas that require deicing.

Reductions in de-icer application have been achieved through highway design, such as snow fences, from improved weather forecasting and ice prediction that allows more targeted applications in space and time, and by measurement of residual salt loadings, so that less salt is used when topping up. Because salt is corrosive, not only to vehicles, but also to critical structures such as bridges, alternative de-icers, most commonly urea and ethylene glycol, may be used on parts of a highway. Theses de-icing chemicals are also used by the aviation industry on runways and aircraft. However, these de-icers also pose a risk to water quality. For example, urea can mobilize metals such as copper, which occur in high concentrations on heavily trafficked roads. Urea also hydrolyses to ammonia, which exerts an oxygen demand on water and, in its un-ionized form, is also toxic. In the aviation industry, the use of urea as a de-icer is being replaced by calcium and magnesium acetate based products.

4.6.2.2 Mitigation of urban pollution

The areal nature of diffuse sources means that they are much harder to control than point sources which are amenable to end of pipe treatment. Urban diffuse sources are particularly challenging, as cities are highly heterogeneous in terms of land cover, land use, and intensity of activity (e.g. housing density, traffic flow on roads), making effective targeting of mitigation measures more difficult. Such measures are of two fundamental types; structural and non-structural. In the USA both are covered by the term Best Management Practices (BMP) while in the UK, the structural measures are known as Sustainable Urban Drainage Systems (SUDS). The term source control is also commonly used, and recognises that BMPs and SUDS are most effective when applied close to the source of stormwater.

The philosophy behind SUDS, is that they act to reintroduce a more natural hydrological regime to the urban environment through detention and retention of storm discharges, through a variety of physical devices (Table 4.6; see also Chapter 3). The term ‘SUDS triangle’ is often used to denote the primary benefits SUDS offer. First, attenuation of storm discharge leads to reduced flood risk, and enhanced ground water replenishment and dry weather flow. Second, this discharge attenuation gives more time for pollutant degradation through natural processes of **volatilisation**, sedimentation and filtration, precipitation, adsorption, **photolysis**, microbial degradation, and plant uptake. Finally, SUDS that include natural elements in their structure are able to enhance the biodiversity and amenity value of buildings and urban areas. The carbon sequestration function of vegetated SUDS is also now recognised as a valuable additional benefit given the importance of climate change mitigation.

Table 4.6 Typical SUDS devices

Position in control hierarchy	**Typical SUDS devices**
Source controls - control runoff at or very near the source	Green roofs (can be extensive or intensive) Downpipe storage (water butts) Infiltration devices (soakaways, filter strips, infiltration trenches, pervious pavements)
Site controls – used to manage water in a localised area. Often convey water from source to regional controls, or promote local infiltration	Swales (broad grassed channels) Infiltration basins (dry depression storage) Balancing pond (wet depression storage)
Regional controls – manage water from one or more sites	Wet pond (primarily for flow attenuation) Constructed wetland (primarily for water quality)

SUDS differ in performance with respect to the main benefits they offer. While most offer multiple benefits, some perform particularly well with respect to flow attenuation, and others with respect to water quality remediation, or ecological performance. This gives rise to a concept known as ‘the treatment train’ in which SUDS are developed in series, so as to maximise the benefits on offer from source to final discharge (whether water course or sewer). Thus a development might have green roofs at the building level, infiltration trenches and swales at the site level, and ponds or wetland at the regional (neighbourhood) level. This approach builds robustness into the treatment of storm water, as it increases the range of pollutant remediation processes at work, and should one SUDS device fail, others are there to treat the runoff.

SUDS do pose particular problems, but these are now better understood and addressed. For example, safety fears with respect to urban ponds are tackled by careful design and edge planting; concerns over maintenance costs have been allayed as experience shows that whole life cycle costs are comparable to or less than that of conventional sewers; and a growing body of evidence on the performance of SUDS (both quality and quantity) means that SUDS designers are better able to develop urban drainage for new sites that meets specified performance criteria.

Although SUDS have received much attention, the importance of non-structural BMPS in urban storm water management must be recognised. These are measures designed to prevent discharge of polluted storm water, and should sit above source control in the BMP hierarchy. These include a very wide range of ‘good housekeeping’ measures, such as street sweeping, rainwater harvesting and re-use, using bunded tanks for storing hazardous materials, covering material in goods yards that might otherwise be washed to drains during rainfall, and having dedicated loading areas where a spill will not drain to a watercourse. Such measures can be incorporated into a site’s environmental management plan, which may be a legal requirement of a consent to develop.

BMPs and SUDS are increasingly required by planning authorities as a condition of development consent. In the UK, for example, local planning policy is driven by national water management policies designed to address surface water quality objectives and flood risk. However, whilst BMPs are rightly considered essential, it is unlikely that they will lead to the restoration of urban river quality just yet. There are several reasons for this. Firstly, the rate of SUDS implementation remains low. For example, a 2009 survey indicated that in Greater Manchester, England, an area of 1100 km^2 with a population of 2.5 million people, there were only 36 SUDS sites in operation (White and Alacon, 2009). Second, where SUDS are installed the primary motivation is usually mitigation of flood risk, which poses the greater threat to human well being. SUDS installed specifically for water quality reasons tend to be installed only to protect the most sensitive receiving waters. Third, SUDS are being implemented principally in a new urban development scheme which does nothing to combat the legacy effects of the existing built environment. Building stock renewal in developing countries is typically less than 1 % a year, so most homes we will be inhabiting in 2050 are already here, hence there is a strong need to retrofit SUDS in the existing built environment. This is more challenging than for new build, but ongoing research and case studies indicates it is feasible (SNIFFER, 2006). Even high density neighbourhoods offer opportunity for SUDS retrofit, through green roofs and devices such as infiltration trenches that occupy little surface space. Of course, funds for retrofit are limited, so knowing where to install SUDS for the greatest benefit is a key requirement.

SUDS are part of a wider goal of developing sustainable urban drainage, which has the main objectives of maintaining an effective public health barrier, avoiding flooding and pollution, and minimising the use of resources, all in a socially acceptable manner. Strategies for achieving this goal include not mixing storm water and wastewater (e.g. via SUDS), not mixing wastewater with clean water (e.g. via water conservation, grey water recycling, and use of no or zero flush toilets), and not mixing industrial and domestic wastes (e.g. via on-site commercial wastewater treatment) which makes effective treatment very difficult. Strategies such as these can add robustness to the urban system. For example, following these strategies should make it easier to deal with novel pollutants in domestic wastewater that arise from the use of pharmaceuticals and personal care products, which via CSOs find their way untreated to urban rivers. However, the transition to a more sustainable system will present problems to be overcome, as evidenced by the difficulties experienced in adequately flushing sewer deposits as SUDS reduce sewer flows.

Clearly, SUDS are just one approach to delivering a more sustainable urban drainage system. Other technical measures exist that improve the operation of the conventional sewer system. These include partial treatment of wastewater in sewer, through the use of aeration, biofilm plates and activated sludge sites (see Chapter 9); real time control of sewers, so that free capacity can be used to store water in sewer and release back to treatment works after the storm event; and real time control of discharge to river, to make best use of natural assimilative capacities.

Arguably, the main challenges facing the quality of urban rivers relate to the need for more integrated and radical solutions. The SUDS triangle neatly illustrates scope for addressing multiple objectives within the area of source control, but integration must be broader than this. Urban areas cannot be considered in isolation from the wider catchment, as too often happens. If programmes of measures to improve water quality (e.g. as required by the EU Water Framework Directive) are to be cost-effective, we must know the source area loading throughout the catchment, the risk that these spatially defined loadings pose to water quality and ecological objectives, and the cost and efficacy of different interventions, whether technical, regulatory (e.g. enforced rules on urban design, commercial activities etc), economic (e.g. raising tariffs for storm water disposal), or educational.

Integration can mean operating within a single sector, finding the best mix of interventions to deliver urban water objectives, but it must also be seen as a cross sector approach too, applied at both project and strategy levels. This could mean, for example, incorporating water quality issues in traffic management (as already done for air quality), working with car manufacturers to promote the use of more benign materials and reduce road sourced pollution, or working with planners and urban designers so that city compaction to reduce travel and carbon emissions does not constrain delivery of SUDS benefits and exacerbate flooding. Thus while SUDS have a role to play in restoring urban river water quality, arguably a greater one than they are currently given, they are only part of the solution, which requires management of multiple sources using multiple tools, both structural and non-structural in nature. Much good work is underway, particularly in terms of research and demonstration sites that gives cause for optimism that more sustainable urban drainage can be delivered.

4.6.3 Acid mine drainage

4.6.3.1 Origins and processes generating pollution from mines

The pollution of surface waters from mines is a problem wherever mineral ores have been exploited. It is a problem throughout the world including: China (He *et al.*, 1997); North America (Wren and Stephenson, 1991; Denicola and Stapleton, 2002); South America (Van Damme *et al.*, 2008); and Australia (Battaglia, 2005). In England and Wales, there are over 300 abandoned mines with discharges which impact on more than 700 km of streams and rivers. Mines which have been abandoned more commonly pose a greater problem than those that are still in operation, this is because working mines are dewatered by pumps (Younger, 2000). When mines are abandoned, dewatering ceases and a process of water table rebound occurs which floods the exposed mine workings. When the water table reaches the surface it emerges as springs, **adits** or surface seepage.

[Insert Figure 4.13 near here]

The activities of mining coal and minerals and mine dewatering exposes underground pyrite-(FeS_2) bearing rock strata to oxygen. In the presence of oxygen and water pyrite becomes oxidised into ferrous sulphate and sulphuric acid. Ferrous sulphate is further oxidised to ferric sulphate this then reacts with water to produce more acidity and ferric hydroxide (Box 4.5). The oxidation of the reduced forms of iron and sulphur is very slow. However, in the presence of acidophilic chemosynthetic bacteria the reactions are accelerated up to a million times. Bacteria which flourish at low pH, such as *Thiobaccilus ferroxidans* (Singer and Stumm, 1970) and *Thiobacillus thiooxidans* and *Metallogenium* (Kleinmann *et al.,* 1981), oxidise iron and sulphate respectively.

BOX 4.5

CONTEMPORARY CHALLENGES

Formation of acid mine drainage

The following chemical reactions summarise the formation of acid mine drainage (Kelly, 1998):

$$FeS_2 + 7/2\ O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2+} \qquad (1)$$

$$Fe^{2}+ + ¼\ O_2 + H^{+} \longrightarrow Fe^{3+} + ½\ H_2O \qquad (2)$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)^{2} + 3H^{+} \qquad (3)$$

$$FeS_2 + 14Fe^{3+} + H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2+} + 16H^{+} \qquad (4)$$

Reaction (1) shows the dissociation of iron pyrite (in the presence of oxygen and water). Pyrite breaks down to form sulphuric acid (SO_4^{2+}) and ferrous iron (Fe^{2+}). When surface waters combine with mine waters the ferrous iron (Fe^{2+}) it forms the ferric variety (Fe^{3+}) (2); a cycle is then established between these two reactions. The Fe^{3+} then further reacts with the available pyrite to form additional acidity, ferrous and sulphate ions (4). The oxygenation of Fe^{2+} is the rate-determining step because reaction 2 is significantly slower than reaction 1.

4.6.3.2 Environmental consequences of mine pollution

Physico-chemical consequences

The waters that emerge from mines into receiving surface waters are very variable in chemical composition (Table 4.7) and may depend on the type of mine and the nature of the surrounding geology. They can be acidic and laden with suspended solids and dissolved metals (Gray, 1997). Indeed, they are frequently described as discharges of acid mine drainage. However, although many discharges are acidic, it is not a universal characteristic and in some cases they may be neutral or basic if the surrounding geology is high in carbonates and able to afford some neutralisation (Kelly, 1988; Schmiermund and Drodz, 1997). The contaminants lead to an increase in the acidity, turbidity, sedimentation, and heavy metal concentrations of the receiving water body. They precipitate out as a coloured flocculate, known as ochre, which stains the substrate of receiving waters (e.g. Figure 4.13). Ochre can vary in colour from yellow to orange-brown.

Table 4.7 Some chemical data from mine discharges.

Chemical parameter	A	B	C	D
pH	2.7	5.3	3.81	7.75
Conductivity (μS cm^{-1})	2590	295	2605	5571
Sulphate*	680	324	1850	3110
Iron*	493	29.04	165	43.7
Aluminium*	59.2	0.25	76	0.03
Zinc*	1.22	0.05	33	0.26
Lead*	-	0.03		-
Copper*	0.06	0.04	1.8	-
Cadmium (μgl^{-1})	<0.005	-	49	-
Suspended Solids*	3158	-	-	-

*Readings in mg L^{-1}

(A) Caulfield mine discharge, Pennsylvania, USA (Letterman & Mitsch,1978).
(B) Stoney Heap coalmine water discharge, Durham, UK (Jarvis and Younger, 1997).
(C) Ballymurtagh mine water discharge, (Gray, 1998).
(D) Whittle Colliery mine water discharge, (Batty *et al.*, 2005).

It is difficult to predict the duration and chemical composition of mine water contamination. Younger (1997) separated the impacts into vestigial and juvenile components. Vestigial acidity is that acquired during the water table rebound phase and in theory should decline exponentially with time with **asymptote** levels (where the curve of the line flattens out and almost reaches zero) being achieved 40 years after the initial discharge. Juvenile acidity arises from the fluctuation of the water table and may persist for centuries.

Biological and ecological consequences

The impact of mine drainage contamination on aquatic ecosystems has been studied extensively. Processes of decomposition can be affected by mine drainage. Bacteria, fungi and decomposing invertebrates can be inhibited from colonising leaf litter and consequently reducing the rates of breakdown (Gray and Ward, 1983). Ferreira de Silva *et al.* (2009) reported that diatoms were rare at a location stressed by mine drainage with high levels of cadmium, lead, and zinc. However, increased diversity and species richness was observed 6 km downstream of the impact. In Lynx Creek, Arizona, algal communities impacted by mine pollution exhibited reduced species richness compared to locations upstream and those in areas of substantial recovery downstream (Lampkin and Sommerfield, 1982). Koryak and Reilly (1984) observed reduced growth of the aquatic macrophyte *Justica america* as a consequence of coal mine pollution in Ohio. Tremaine and Mills (1991) recorded that protozoan abundance and grazing rates on bacteria were substantially reduced in a lake affected by acid mine drainage. The impact on benthic invertebrates is widely reported with reduced abundances, species richness and diversity being common factors. Communities in riffle habitats appear to be affected more than those in pool habitats (Van Damme *et al.,* 2008). Furthermore, species belonging to the Orders Ephemeroptera and Plecoptera also appear to be those most affected (Clements, 1994). Letterman and Mitsch (1978) noted that the standing crop of fish communities declined downstream of mine drainage on Ben's Creek, Pennsylvania, from 228.2 kg ha^{-1} to 11.2 kg ha^{-1}. The sculpin, *Cottus bairdi*, showed the greatest decline from 151.2 kg ha^{-1} to 0.3 kg ha^{-1}.

Social and economic consequences

The human impacts of mine drainage pollution are many and varied. Possible consequences include: reduced water availability for abstraction for public supply from both ground water and surface water sources; surface waters unsuitable for irrigation and livestock watering; contamination of navigational rivers and canals, for both commercial and recreational use, impacts upon the maintenance of the navigational area and the waterborne craft; ecological damage can reduce the recreational potential for commercial fisheries and angling; and the general recreational and amenity value of watercourses are affected by the visual and aesthetic impact of highly coloured ferruginous mine waters.

4.6.3.3 Mitigation of mine pollution

The reduction of the impact of mine water pollution falls into three types of system: physical, chemical and biological. Physical systems involve water oxidation through impoundment and cascades to facilitate the settlement of the contaminants into sludge (Diamond *et al*., 1993). The costs of these systems can be high as they require both high capital investment in terms of construction costs and there are further revenue costs from the disposal of the resultant sludge. Chemical systems use the addition of chemicals to actively promote the decontamination of the water. Examples typically include the addition of lime to produce flocculation and settlement of contaminants followed by pH neutralisation (Chadwick *et al*., 1986). Although capital costs are much reduced they are expensive to run because of the costs of the treatment chemicals and sludge disposal. Biological systems are dominated by the construction of semi-natural or artificial habitats (Figure 4.14) which facilitate bacterial activity to reduce contaminants through reed beds and wetlands (Webb *et al.,* 1998). These systems are relatively cheap to construct and run. Furthermore, the ecological principles behind them also suggest that they may be a sustainable solution to mine drainage pollution (Kalin, 2004). However, such a solution requires the availability of suitable land areas close to the source of pollution and this is not always possible.

[Insert Figure 4.14 near here]

In reality, combinations and overlaps of treatment processes are frequently observed. For example, the mine remediation treatment at Bullhouse on the River Don in Yorkshire involves a physical settlement lagoon and a wetland area (Laine and Dudeney, 2000). Such systems can result in significant reductions in loadings of metals. The Bullhouse scheme illustrates this with iron being most effectively removed (Table 4.8). Wiseman *et al.* (2003)

also noted similar reductions in iron loading (82 % to 95 %) on the River Pelenna in South Wales. Furthermore, ecological recovery has also been observed in the Pelenna study with the return of sensitive invertebrate species (e.g. the mayfly *Empherella ignita*), brown trout (*Salmo trutta*) and birds such dippers (*Cinclus cinclus*).

Table 4.8 Changes in typical chemical composition of the Bullhouse mine discharge into the River Don, Yorkshire, UK, before (A) and after (B) remediation (data sourced from Laine and Dudeney, 2000)

Chemical parameter	A	B
pH	5.9	5.9
Conductivity (μS cm^{-1})	442	281
Sulphate*	788	475
Iron*	54.6	2.7
Aluminium*	2.31	0.32
Zinc*	91.5	65.3
Lead*	0.147	0.049
Copper*	0.0202	0.0042
Cadmium (μgl^{-1})	-	0.28
Suspended Solids*	16	11

*Readings in mg L^{-1}

4.6.4 Atmospheric pollution

4.6.4.1 Source of acid rain

Over than last 100 years, there have been significant changes to global atmospheric chemistry. The major atmospheric pollutants include acidifiers such as sulphur dioxide (SO_2) and nitrogen oxides (NO_x); toxic substances such as ozone, volatile organic compounds (VOCs) and heavy metals; and fertilizing substances such as ammonia (NH_3) and nitrous oxides NO_x. The amount of acidifying pollutants present in the atmosphere has been affected by an increase in the combustion of fossil fuels, changes in agricultural practices and, more recently, by the introduction of new legislation to reduce emissions to the atmosphere (e.g. the 1999 Gothenburg Protocol which set emission ceilings for 2010 for sulphur, NO_x, VOCs and ammonia).

Rainfall is naturally acidic, with a pH of about 5.6, due to its equilibrium with carbon dioxide in the atmosphere:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

However, the pH of rain decreases as the amount of SO_2 and NO_x in the atmosphere increase. Acid rain is generated from the oxidation of SO_2 and NO_x to H_2SO_4 and HNO_3, respectively. Acid rain can be carried great distances in the atmosphere, not just between countries but also from continent to continent. Hence the impact of acid rain on freshwater ecosystems can be far from its source.

4.6.4.2 Impact of acid rain on surface water

In the 1960s and 1970s, observations of an increase in surface water acidity leading to a decline in the salmon population across areas of Southern Scandinavia were widely reported in the media. However, much research was required to establish the cause-effect relationship between acid rain and surface water acidification. **Palaeolimnological** techniques that reconstructed pH based on diatoms in lake sediment cores allowed the chemical histories of a large number of lakes across Britain, Scandinavia, north-east USA and Canada to be evaluated (Battarbee *et al.,* 1990). This showed that lakes, in areas with base-poor geology that had received high rates of acidic deposition had experienced significant acidification.

The effect of surface water acidification on the aquatic flora and fauna is pronounced (e.g. Schindler, 1988). The affects on aquatic biota can be direct such as toxicity associated with changes in water chemistry or indirect such as changes in habitat or food availability. Acidification also increases the solubility of heavy metals, such as aluminium, manganese, lead, cadmium and zinc, many of which are toxic to aquatic organisms. For example, acidity and high concentrations of aluminium (Al^{3+}) can lead to deterioration of aquatic life with losses in the diversity and size of invertebrate and fish populations. At pH less than 5, aluminium is soluble and leached from the soil to surface waters as Al^{3+}. The toxicity of Al^{3+} has been mainly studied with reference to fish; at concentrations $< 100\ \mu g\ L^{-1}$, it affects the **osmoregulation** of fish (i.e. their ability to regulate the amount of salt and water within their body) and at concentrations $> 100\ \mu g\ L^{-1}$ a gelatinous precipitate of aluminium hydroxide ($Al(OH)_3$) forms on their gills leading to suffocation (Jackson and Jackson, 2000). Changes in the population of the dipper *Cinclus cinclus*, a riparian bird, in areas that experienced stream water acidification such as mid-Wales (Tyler and Ormerod, 1992), is an example of indirect effect of acidification on aquatic biota.

The susceptibility of a particular surface water body to pollution from acid rain depends on its capacity to act as a buffer and neutralise the effects of acid rain. This capacity is largely determined by the chemical properties of surrounding geology and soil type. Rocks and soils that contain large amounts of base cations (bases are substances that can accept hydrogen ions (protons) and are the opposite to acids), such as calcium and magnesium, have a high **buffering capacity**. In addition, surface water bodies in chalk or limestone regions are able to buffer the increase in hydrogen ions (H^+) due to the presence of bicarbonate anions (HCO_3^-):

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow H_2O + CO_2$$

In contrast, water bodies underlain by base-poor igneous (e.g. granite) or ancient metamorphic rocks have a lower buffering capacity. Soil development on such lithologies generally results in thin, base poor soils with a small base cation pool and slow release of base cation from the weathering of the bedrock. Base cation stores in such soils are rapidly depleted in response to incoming acidic rain resulting in the acidification of soils and surface waters. Hence areas dominated by igneous and metamorphic rocks and receive high annual rainfalls that are acidic are particularly vulnerable, such as the Canadian shield, the Appalachians of America and the mountains of Scandinavia and western Britain. This differential ability of surface waters to cope with acid rain has been examined through use of a '**critical loads**' approach as discussed in Box 4.6.

Box 4.6

TECHNIQUES

Evaluating the acidification status of surface waters: the critical load approach

The concept of the critical loads approach is based on a "dose-response" relationship and has been widely applied to addressing pollution problems (Fenn, 2011). A critical load can be defined as a "quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988). The critical load of acidity for a freshwater resource is exceeded when the total amount of acid deposition is greater than the ability of the system to neutralise the deposited acidity. Two models have been widely used in critical loads for surface waters; the steady-state water chemistry (SSWC) model (Henriksen *et al.*, 1992) and the first–order acidity balance (FAB) model (Posch *et al.,* 1997). Both models provide an estimate of the level of acid deposition below which the **acid neutralising capacity** (**ANC**) will remain above a pre-determined level. Acid neutralizing capacity (ANC), measured in microequivalents per litre ($\mu eq\ L^{-1}$), is a commonly used chemical indicator of sensitivity to acidification as it characterizes the ability of water to neutralize strong acids including those introduced by atmospheric deposition and it can be linked to biotic response thresholds such as the health and condition of aquatic biota. Current UK and European critical load applications use the FAB model and in the UK an ANC limit of 20 μeq L^{-1} is applied to all sites, except those which are believed to be naturally acidic where a value of ANC = 0 μeq L^{-1} has been used.

The acidity critical loads for UK freshwaters are based on data from a national survey of lakes or headwater streams, where a single site, judged to be the most sensitive (in terms of acidification) was sampled in each 10 km grid square of the country. In less sensitive regions (e.g. south-east England) the sampling generally consisted of one site in each 20 km grid square. In 2004 this "mapping dataset" was updated to include sites from other surveys and networks, where appropriate data were available. To date the FAB model has been applied to 1595 sites in Great Britain and 127 in Northern Ireland. Hence the freshwater critical load maps do not represent all waters in the UK and the results are mapped by site location (Figure 4.15). The critical load for freshwaters is expressed in terms of three terms; CLmaxS, CLmaxN and CLminN, where CLmaxS is the critical load of acidity expressed in terms of sulphur only (i.e. where nitrogen (N) deposition is zero), CLmaxN is the critical load of acidity expressed in terms of N only (i.e. where S deposition is zero) and CLminN represents the long-term N removal processes (e.g. N uptake and immobilisation), i.e. the amount N that can be depostioed before it will begin to contribute to surface water acidification (see Henriksen and Posch (2001) for more detail). Because both S and N compounds can contribute to the exceedance of the acidity critical load, these three 'acidity' critical loads parameters are required to determine the combinations of deposition that will not exceed the critical load. In general, the lower the values of CLmaxS and CLmaxN the more sensitive the sites are to acidification from atmospheric deposition. In summary, critical loads have been successfully develop and implemented in Europe, and other areas, for assessing the impacts of air pollution on essential ecosystem services and for informing public policy for reductions in air pollution emissions.

[Insert Figure 4.15 in here]

4.6.4.3 Recovery from surface-water acidification

Since the 1980s considerable national and international effort has been made to decrease emissions of acidifying pollutants. This has been challenging since those countries suffering most from acid rain are not always the main polluters. In 1979, 34 European and North American countries adopted the Convention on Long-Range Transboundary Air Pollution, which bound them to reducing emissions. The convention agreed firm targets in 1983, when 21 European countries agreed to reduce their SO_2 emissions by 30 % from the 1980 levels by 1993. Twelve countries reached this target by 1988. The UK did not ratify this agreement, but did eventually declare an intention to reduce SO_2 emissions by 30 % in the late 1990s. In the United States, an ‘Acid Rain Program’ commenced in 1995 that aimed to achieve environmental and public health benefits through reductions in emissions of SO_2 and oxides of nitrogen (NO_x). Since the signing of these agreements there has been a substantial reduction in SO_2 emissions in Western Europe, although emissions of NO_x continued to increase until the late 1980s before starting to decline.

In the UK, sulphur deposition declined by 60 % between 1986 and 2005 (Fowler *et al.*, 2005). The response of surface waters to this decline in sulphur deposition has been monitored via the UK Acid Water Monitoring Network (AWMN). The decline in sulphur deposition has resulted in a significant decline in the sulphate concentration of upland waters (Davies *et al.,* 2005), and the majority of AWMN sites also display an increasing trend in pH, alkalinity and acid neutralizing capacity (Monteith and Evans, 2005). Data from the International UN monitoring program ICP Waters (International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes) for 12 regions of Europe and North America, also display similar declines in sulphate concentrations and increases in alkalinity and pH (Skjelkvale *et al*., 2005) in response to decline in sulphur deposition.

Both the UK AWMN and ICP Waters Programme reported an increase in surface water dissolved organic carbon (DOC) concentrations over the period 1990-2005 (Freeman *et al*., 2001; Skjelkvale *et al.,* 2005), with concentrations doubling across the UK AWMN (Evans *et al.,* 2006). This trend has raised concerns about the provision of safe drinking water (Holden *et al.,* 2007) and the stability of soil carbon stores (Freeman *et al*., 2001; Bellamy *et al.,* 2005). A range of different hypotheses have been proposed to explain this trend, including those linked to climate change (e.g. increase in temperature, changes in distribution and volume of rainfall and elevated atmospheric carbon dioxide (Freeman *et al.,* 2001; 2004)), changes in land management (e.g. Yallop *et al.,* 2009) and recovery from acid rain (Evans *et al*., 2006). Using data from the ICP Waters Programme and UK AWMN, Monteith *et al.* (2007) demonstrated that the spatial variation in DOC trends could be explained by a simple model based on changes in the chemistry of atmospheric deposition (predominantly SO_4 and Cl). This study provided strong support for the hypothesis that reduction in the emissions of SO_2 over the last 20 years is the primary cause on the increasing trend in surface water DOC and, therefore, implied that these systems may simply be returning to their preindustrial conditions. Thus, rising DOC concentrations in freshwaters may to a large extent reflect recovery from the effects of acid deposition, rather than ecosystem degradation in response to climate or land use change.

While sulphur deposition has declined rapidly over the last 20 years, atmospheric deposition of reactive N compounds have shown much smaller changes; reduced N and wet deposition of nitrate have declined by only 10 % in the UK (Fowler *et al.,* 2005). Where N deposition exceeds the biological demand of the terrestrial ecosystem (termed N saturation), the excess N is removed in drainage water. This increased N leaching can lead to acidification of surface waters, when the NO_3 is accompanied by Al^{3+} or H^+, and eutrophication, where N is the limiting nutrient. However, identifying the precise impact of increased N leaching on aquatic ecosystems is complicated by the variety of chemical forms in which N may exist in atmospheric deposition, terrestrial biomass and surface waters. In addition, a variety of terrestrial processes separate N deposition from its effects and reduces the ability to attribute observations of aquatic effects to known rates of deposition. The ratio of NO_3:(NO_3 +SO_4) in surface waters provides an index of the influence of NO_3 on chronic acidification status, assuming that both anions are derived from anthropogenic acid deposition. A value of greater than 0.5 indicates that NO_3 has a greater influence on the acidification of surface water than SO_4. Ratios of NO_3:(NO_3 +SO_4) in lakes and streams of acid sensitive regions of Europe and North America in the 1980s and 1990s were generally low (<0.3) with typically <15% of the acidity explained by NO_3 (Chapman and Edwards, 1999). However, Curtis *et al.* (2005) showed that as S deposition decreases, and if N deposition remains static and the ability of a catchment to store atmospheric N is exceeded, increased NO_3 leaching at the UK AWMN may counterbalance any reduction in SO_4 due to reduction in emissions of SO_2, resulting in little change or even a decrease in the acidity of surface waters over the longer term.

Reflective question

What methods can be adopted to reduce pollution from agriculture, urban areas and mine drainage?

4.7 The future

Over the last century different strategies have been developed to overcome the conflict between water quality deterioration due to human activities and water use that includes a combination of:

1. Wastes treated before discharging to a water body.
2. Waters treated in order to meet specific water quality requirements (e.g. drinking water).

3. Water quality determined and procedures adopted that prevent deterioration (e.g. land management options).

In most countries these strategies have been accompanied by the development of laws and regulation to help to prevent and reduce water pollution. For example, in the United States there is the 1972 Clean water Act and the 1974 Safe Drinking Water Act. However, one of the biggest problems with water pollution is its transboundary nature. Many rivers cross countries, so pollution discharged in one country can cause water quality problems in neighbouring countries. While environmental legislation in one country can make it tougher for people to pollute, to be really effective these laws need to operate across national and international borders (see Chapter 11). The European Union has water-protection laws (known as directives) that apply to all of its member states. They include, for example, the 1976 Bathing Water Directive (updated 2006), which seeks to ensure the quality of the waters that people use for recreation. More recently the European Union has introduced the Water Framework Directive (WFD) that has the following key aims:

- Expand the scope of water protection to all waters, surface waters and groundwater
- For all inland waters to achieve "good ecological status" by a set date
- Water management to be based on river basins
- "Combined approach" of emission limit values and quality standards
- Getting the price right
- Getting the citizen involved more closely
- Streamlining legislation

The Directive requires the establishment of river basin districts, some of which will traverse national boundaries, and for each of these a ‘River Basin Management Plan’ that will be updated every six years. There are four distinct elements to the river basin planning cycle: characterisation and assessment of impacts on river basin districts; environmental monitoring;

the setting of environmental objectives; and the design and implementation of the programme of measures needed to achieve them. However, in England and Wales, it was estimated in 2008 that approximately a fifth of all river water bodies are at risk or probably at risk of failing to reach ‘good ecological status’ by 2015 due to pollution from point sources, while over 85 % of surface water bodies are currently at risk or probably at risk of failing to reach ‘good ecological status’ because of diffuse pollution. While the WFD has set stringent targets for achieving ‘good ecological status’ of all surface waters, it is important to remember that surface waters have been used and degraded by man over decadal and centennial timescales, and thus the 2015 WFD targets need to be considered against these longer timescales of system response.

To date studies investigating the impact of climate change on the global water cycle have concentrated on water resources and water supply. Hence there is currently much uncertainty about the potential impacts of climate change on surface water quality. In their comprehensive review of the potential impact of climate change on river water quality, from a UK perspective, Whitehead *et al.* (2009) make the following key points:

1) The IPCC Fourth Assessment Report (IPCC, 2007) had a relatively short section on the potential impacts of climate change on river water quality.
2) The most immediate response to climate change is expected to be an increase in river and lake water temperatures that will result in changes in water quality (e.g. concentration of dissolve oxygen, and ecology – see Chapter 6).
3) Changes in the timing, intensity and duration of precipitation will lead to changes in flow regime that will affect water quality and ecology. However, there is a lot of uncertainty about the likely impacts due to changes in regional precipitation.

4) Lower river flows will result in less volume available for dilution of pollution downstream of point discharges.
5) Increased storm events, especially in summer, would lead to more frequent incidences of combined sewer overflows, discharging highly polluted waters into receiving water bodies.
6) More intense rainfall and flooding could result in increased suspended solids, sediment yields and associated contaminant metal fluxes.
7) Nutrient loads are expected to increase.
8) There is a need for models to represent the whole ecosystem and the uncertainty in model prediction quantified.

Overall, climate change studies, especially in relation to water quality and ecology, are at fairly early stages and the outcomes are subject to considerable uncertainty (Whitehead *et al.*, 2009). Hence more research is required in this area.

Some people believe that global changes in population and economic development will have a much larger impact on water supply and quality than will changes in climate over the next few decades (e.g. Vörösmarty *et al.*, 2000 and see Chapter 2). With more people now living in cities than rural areas, and with an estimated growth in the urban population of 1.5 billion over the next 20 years (UNPD, 2007), providing safe drinking water to urban inhabitants is a major challenge. In cities, with large upstream populations, the risk of drinking water containing high concentrations of nutrients and bacteria are high. A recent study showed that the number of people living in cities with an upstream population density of 19 people per hectare was 53 million, all in Africa and Asia. 890 million people live in cities with an upstream population density greater than 5.5 people per hectare (McDonald *et al.*, 2011). Where these cities have adequate resources, they are able to treat the polluted water before distribution to the urban population. However, most cities in the developing world are unable to afford water treatment and are reliant on international aid or loans to build water treatment plants and sewage treatment works (McDonald *et al*., 2011). The lack of sewage systems in villages and towns upstream of cities has serious consequences for drinking water quality downstream. Other ways of improving water quality in rivers entering cities is to change land use or management upstream. To obtain a better understanding of how surface water quality will change in the future an integrated approach is required that brings together the climate change, water and land users and socio-economic communities. There is also a need to mobilise financial resources, particularly in the developing world, to support integrated approaches to improving water quality (see Chapter 8).

Reflective question

How might climate change impact water quality?

4.8 Summary

Rivers and lakes are vital natural resources; they provide drinking water, habitats for many different types of flora and fauna, and are an important resource for industry and recreation. However, due to human activities a significant proportion of them are now polluted or under threat from pollution (e.g. Vörösmarty *et al*., 2010). Protecting and improving the aquatic environment is an important part of achieving sustainable development and is vital for the long term health and well being of humans and wildlife.

The hydrological pathway by which water travels through a watershed has a large control on the solute concentration. For example, water that passes rapidly over or though the watershed has a lower solute content than water that has slowly moved through the watershed.

Temperature, redox potential and pH have a strong control on the form and oxidation state of different solutes. Global and regional patterns in surface water chemistry are predominantly controlled by differences in geology and climate, with soil, vegetation and land use being more important controls at the local scale. Surface water chemistry also displays temporal patterns at a range of scales from diurnal to seasonal to long-term. These temporal patterns arise due to the processes controlling the supply of solutes available for leaching varying over time and secondly the hydrological processes that generate runoff within a catchment are dynamic and vary with climate and season.

Surface water chemistry is directly threatened by human activities. River and lake chemistry is affected by widespread land cover change, irrigation, urbanisation, industrialisation and its legacy, engineering schemes like reservoirs, and pollution from atmospheric deposition. Legislation, population growth and climate change may all influence surface water chemistry in the future.

Further reading

Campbell, N., D'Arcy, B., Frost, A., Novotny, V. and Sansom, A. 2005. *Diffuse Pollution: Theory, Control Measures, Practical Experiences*. IWA Publishing; London.

This is an introductory text covering the nature, causes and the significance of urban and rural diffuse pollution. Best management practices to tackle the problems are examined as are the ways in which the adoption of such practices may be brought about. It makes use of case studies, from an EU perspective, to examine the strengths and weaknesses of various approaches, including SUDS.

Haygarth, P. and Jarvis, S. 2002. *Agriculture, hydrology and water quality*. CABI Publishing; Wallingford, Oxfordshire, UK.

This book contains a collection of review articles of global problems of diffuse water pollution from agriculture, which affects the water quality of surface waters and the oceans.

Issues in Ecology (http://www.esa.org/science_resources/issues_ecology.php)

These reports present the consensus of a panel of scientific experts on issues relevant to the environment and are written in a language understandable by non-scientists. Relevant reports include 'Nonpoint pollution of surface waters with phosphorus and nitrogen' and 'Impact of atmospheric pollution on aquatic ecosystems'.

Kelly, M. 1988. *Mining and the freshwater environment*. Elsevier Applied Science; London.

Although this book concentrates to a significant extent on the impacts of metal mining, it also provides good coverage of the general principles and processes that lead to acid mine drainage and the extent of their impacts on the freshwater environment.

Lawson, E.A. 2000. *Aquatic pollution: An introductory text*. John Wiley and Sons; Chichester.

This book introduces the basic concepts and issues in aquatic pollution. It describes the effects of pollution associated with urban runoff, acid rain, sewage disposal, pesticides, oil spills, nutrient loading, and many more, on lakes, streams, groundwater and oceans.

Novotny V. 2002. *Water quality: Diffuse pollution and watershed management (2nd edition).* John Wiley and Sons, New York.

A comprehensive book that covers the sources and control of a wide range of pollution sources from urban, industrial, and highway pollution to agricultural pollution. It also covers management and restoration of streams, lakes, and watershed management techniques.

Novotny, V. (ed.) 1995. *Nonpoint pollution and urban stormwater management*. Technomic Publication Co.; Lancaster, PA.

This book covers the most important topics and solutions of the diffuse pollution problem from a USA perspective, with emphasis on urban sources and abatement.

Classic papers

O'Connor D. J., 1960. Oxygen balance of an estuary. *Journal of the Sanitary Engineering Division*, ASCE 86: Proceedings Paper 2472.

The foundation of modern water quality modelling for surface waters

Hasler, A. D. 1947. Eutrophication of lakes by domestic drainage. *Ecology* 28: 383–395.

A paper which showed how agricultural and urban pollution could lead to eutrophication and hence lake ecosystems required good land management practice.

Project ideas

- Measure the solutes and sediment concentrations of two tributaries just upstream of a confluence and also measure the same things immediately downstream of the confluence. Have there been chemical changes at the confluence or has the system just mixed?
- In an agricultural catchment sample several tributaries and the main river channel at different points for key nutrient concentrations (e.g. nitrates and phosphates). Can you relate differences to land use?
- Test some water quality variables immediately upstream and downstream of a BMP/SUDS device and evaluate its performance.

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Figure captions

Figure 4.1 The different hydrological pathways that precipitation may take to reach surface waters and their effect on solute concentrations.

Figure 4.2 Eh-pH diagram for the simple ions and hydroxides of iron at atmospheric pressure and 25°C. If the water pH and redox potential are known the figure shows the form of iron present (after Morgan and Stumm, 1965). Reprinted with permission from Elsevier from *Advances in water pollution research, Proceedings of the Second International Conference on Water Pollution Research,* Morgan, J.J. and Stumm, W. The role of multivalent metal oxides in limnological transformations, as exemplified by iron and manganese. Pergamon Press, Oxford, 1, 103–118. Copyright 1965.

Figure 4.3 Relationship between mean annual runoff and (a) discharge weighted mean total dissolved solids concentrations and (b) mean annual dissolved load for a sample of 496 world rivers (after Walling and Webb, 1986; reproduced with permission from Walling, D.E, and Webb, B.W. 1986. Solutes in River Systems. *In*: Trudgill, S.T. (ed) *Solute Processes,* John Wiley and Sons Ltd; Chichester. 251-327).

Figure 4.4 Cross section of a thermally stratified eutrophic lake in summer showing location of the epilimnion, thermocline and hypolimnion and associated changes in temperature, dissolved oxygen and iron and manganese concentrations with depth.

Figure 4.5 The influence of geology and climate on the total dissolved solids (TDS) and major chemical composition of surface waters (adapted from Gibbs (1970) Mechanisms controlling world water chemistry. *Science* 170: 1088-1090. Reprinted with permission of AAAS)

Figure 4.6 Dissolved oxygen concentrations and temperature recorded at 15 minute intervals at a stream in the North Pennines, UK, shows clear diurnal variations (data kindly provided by Katie Aspray, University of Leeds).

Figure 4.7 Changes in stream discharge and silicon and dissolved organic carbon concentrations during a storm event in a headwater stream in NE Scotland (adapted from Stutter *et al*., 2012).

Figure 4.8 Mean monthly concentrations in stream water from the headwaters of the River Tees, northern England (a) calcium, (b) nitrate and (c) dissolved organic carbon (DOC). (data kindly provided by the Environmental Change Network, 2012, citation code: ECN:PC7/12)

Figure 4.9 Long term trends in SO_4, Cl, DOC and pH at the UK Acid Water Monitoring Network (data kindly provided by CEH Lancaster).

Figure 4.10 Slurry being injected to a field by a specialist machine (a) with the deposited slurry shown in (b).

Figure 4.11 Farm advice activities being undertaken as part of the England Catchment Sensitive Farming Delivery Initiative (ECSFDI)

Figure 4.12 Long term NO_3 concentrations and fluxes in the River Stour. (Reprinted (adapted) with permission from Burt, T.P., Howden, N.J.K., Worrall, F., Whelan, M.J. and Bieroza, M. 2011. Nitrate in United Kingdom rivers: policy and its outcomes since 1970.

Environmental, Science and Technology 45: 175-181. Copyright 2010, American Chemical Society).

Figure 4.13 Acid mine discharge at Jackson Bridge on New Mill Dyke, Yorkshire, UK.

Figure 4.14 Semi natural wetland (a) and artificial reed bed wetlands (b) River Pelenna, South Wales, UK.

Figure 4.15 Critical loads exceedance maps for the UK freshwaters in 2004 calculated using the first-order acidity balance (FAB) model (Source: Centre for Ecology and Hydrology, http://cldm.defra.gov.uk).