WATER QUALITY MONITORING AND ASSESSMENT OF GROUNDWATER

Technical Guidance Document

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FOREWORD

This technical guidance document is intended for scientists and practitioners who work with freshwaters in the field and in the laboratory but who do not have specialist knowledge of hydrogeology. It will guide water resource managers in planning and implementing a groundwater monitoring programme that will generate information to support management action and policy development towards sustainable use of groundwater resources.

This document is part of a series of guidebooks that address various aspects of monitoring and assessment of freshwater. It describes the main features of groundwater that govern its quantity, availability and chemical quality. Understanding these features assists in the development of a monitoring programme that will provide information for management and sustainable use. Important principles for monitoring are explained together with methods for obtaining and interpreting water quality data from boreholes and wells. Sources and pathways of contamination in groundwater are discussed,

together with approaches to assessing their impact on the quality of the resource. It is recommended that the other guidebooks in the series are consulted for more detail on other related topics, such as monitoring programme design and quality assurance.

Other guidance documents in the series to be released in 2022 include:

- An Introduction to Freshwater Quality Monitoring and Assessment

- Water Quality Monitoring and Assessment in River, Lakes and Reservoirs

- Quality Assurance for Freshwater Quality Monitoring

- Freshwater Quality Monitoring with Biota

- Freshwater Quality Monitoring using Particulate Matter

Contents

CHAPTER 1

INTRODUCTION

In many countries, groundwater is an essential source of domestic water supplies due to its generally good quality and minimal requirement for treatment prior to use. In arid regions it is often the main or only source of useable freshwater. Even in countries with plentiful surface waters and advanced treatment and distribution systems, groundwater is important for domestic supplies in remote and rural locations that are not served by distribution networks. The limited data available suggest that between 2 per cent and 95 per cent of national water needs are supplied from groundwater, with the higher proportion being used in water-scarce countries (Margut and van der Gun 2013). Globally groundwater accounts for approximately 26 per cent of total water abstractions (WWQA 2021). It is essential that groundwater resources are managed to ensure their quantity and quality meet human needs and support freshwater ecosystems. In arid regions where groundwaters are the main source of freshwater supplies, concern has mainly focussed on the amount of water available and on trying to manage the sustainable use of that water. There is growing evidence, however, that groundwaters are becoming contaminated and no longer meet required quality characteristics, potentially posing a threat to human health (WWQA 2021). The extent and nature of the contamination is unclear, due to the limited monitoring of groundwater quality at a global scale, especially in the Global South (WWQA 2021). In addition, the risk posed to human health from naturally occurring contaminants, such as arsenic and fluoride, are often unknown due to a lack of monitoring (WWQA 2021). Better information and understanding of groundwater will help to guide public health interventions, also in view of how contaminated water affects women, men and children in different ways.

Most groundwater monitoring is focussed on the suitability of the water for drinking water supplies but monitoring programmes should also take into account other uses of groundwater, such as irrigation, ecosystem support and industrial use. The monitoring programmes should, therefore, be targeted and designed accordingly. This guidebook provides fundamental information on the occurrence and behaviour of groundwaters and how to use that information in the development of a groundwater monitoring programme. As for all freshwater monitoring programmes there are a chain of steps that need to be followed (Fig. 1.1) to ensure the programme generates meaningful

Figure 1.1   The chain of activities in designing and implementing a freshwater quality monitoring programme (adapted from Chapman *et al*. 2005)
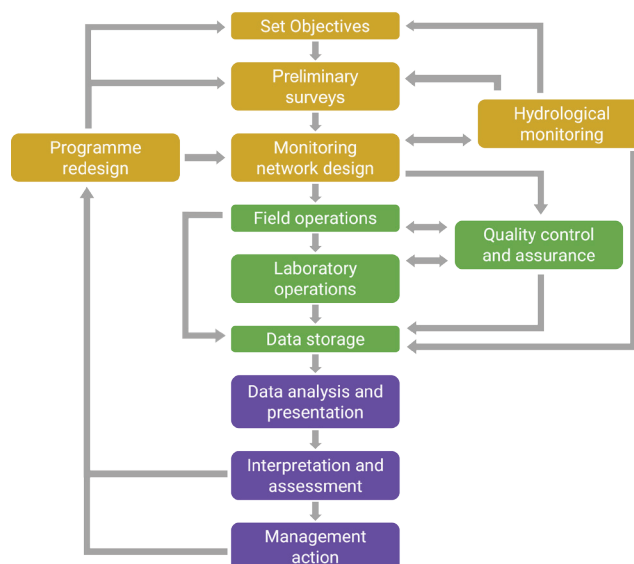
data that will support an assessment of the state of the groundwater resources that, in turn, will inform management and policy. The chain starts with the critical element of defining the objectives of the monitoring programme, i.e., what information it is expected to generate and for what purpose. The design of the programme, i.e., the selection of sampling locations, parameters to be measured (quantity and quality) and the frequency of measurement, will need to ensure that the objectives are met. Looking at existing information and data, as part of a preliminary survey, can save a lot of time and effort by identifying whether existing boreholes can be used for sampling or whether new wells will need to be drilled. Also, as women and girls are often tasked with water collection in developing countries, their intimate knowledge of local conditions is invaluable; thus, engaging with them as key stakeholders in water planning, management and monitoring exercises is crucial.

The results obtained through field and laboratory work need to be stored in a database that facilitates easy access and sharing of the data, in order to facilitate data analysis and presentation in a way that is useful for management purposes. An important element of all water quality monitoring programmes is the application of a quality assurance plan that includes all steps in the data process, from field sampling to laboratory analysis and data storage. A comprehensive quality assurance plan provides confidence in the data and is essential where data are shared between agencies, for example in the case of transboundary groundwaters. This guidebook focusses on the information needed to design a groundwater monitoring programme and to implement the field aspects; laboratory procedures are not covered in detail. Data management and quality assurance for monitoring are the topics of companion guidebooks.

1.1 The hydrological cycle

Only 2.5 per cent of all water on Earth is available for human use in the form of fresh water; the remainder is in the oceans. Most of the freshwater (69.5 per cent) is stored in ice caps and glaciers and another 30.1 per cent is underground. The remainder is stored in lakes

and rivers (0.26 and 0.0057 per cent respectively) and in wetlands and soil and atmosphere moisture (0.13 per cent). The addition of water into groundwater storage is known as recharge. This occurs naturally from precipitation, from surface runoff, and from surface water bodies, such as lakes and reservoirs (Fig. 1.2). In addition, human activities can also make important contributions to recharge as a result of, for example, surplus irrigation, pipe and canal leakage, and aquifer augmentation schemes.

Figure 1.2 The hydrogeological cycle of water between atmosphere, land surface, groundwater and the oceans
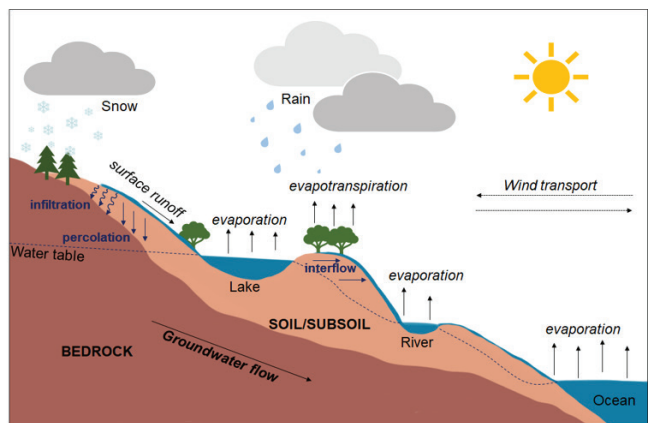
Once water enters the soil through the process of infiltration (see Box 1.1), it can flow in a variety of directions depending on the soil type and other local conditions. In the upper layers of soil and rock, pores and voids are filled with air rather than water. This is known as the unsaturated or vadose zone. In this zone, groundwater tends to flow vertically downwards under the force of gravity. In the saturated or phreatic zone beneath this, all pores and voids are filled with water, and under those circumstances, groundwater movement occurs in response to pressure. Pressure can be induced, for example, by a simple change in elevation, causing flow from higher to lower points. The resultant groundwater flow may intersect the ground surface and emerge as springs or flow back to surface water bodies, from which it may evaporate. Groundwater can also intercept the oceans below sea-level, resulting in the emergence of sub-sea springs. It is also important to note that artificial abstraction for human use constitutes an important form of

BOX 1.1 DEFINITIONS RELATED TO THE MOVEMENT OF UNDERGROUND WATER

Infiltration describes the process of water at the ground surface entering the soil.

Percolation is the term used to describe the vertical water flow from the unsaturated zone into the saturated zone (i.e., into groundwater).

Interflow is the lateral movement of water near the surface, in the unsaturated (vadose) zone. It occurs where a thin layer of soil is underlain by a rock of low porosity.

Groundwater flow is used to describe water flow in the saturated (phreatic) zone.

Groundwater recharge is the water added to an aquifer through percolation.

groundwater discharge (i.e., withdrawal of water from groundwater storage), which can significantly affect the local hydrogeological cycle. Evaporation from rivers and lakes, and particularly from the oceans, provides the main source of atmospheric moisture, together with evaporation of soil moisture or transpiration by plants. The water in the atmosphere is ultimately returned to the Earth's surface by precipitation, completing the cycle. As precipitation reaches the surface, some is intercepted, and some infiltrates into the soil. Infiltration provides the major source of water for groundwater recharge.

1.2 Underground water storage

In a profile view, the unsaturated (vadose) zone is the layer immediately beneath the surface. It can be divided into three separate zones: (i) soil, (ii) intermediate zone, and (iii) capillary fringe (Fig. 1.3), with each of these presenting different water storage characteristics. The saturated (phreatic) zone is the layer immediately below the water table

Figure 1.3   The different underground water storage zones located in the unsaturated and saturated zones
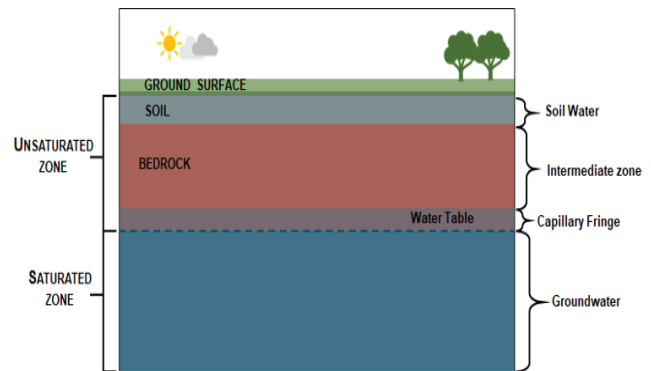
and is the zone from which groundwater is extracted. Therefore, the phreatic zone will be the main subject of this guidebook.

Soil water is contained in the upper topsoil layers of the Earth's surface, i.e., the layer in which plants are rooted and which provides them with moisture and nutrients. Here, the rainfall that infiltrates the soil fills voids between particles and is held there by molecular forces. If all voids are water-filled, the soil is said to be saturated. If a saturated soil is allowed to drain under gravity, which occurs more freely in coarse rather than fine soils, the soil water percolates down into the intermediate zone.

Following rainfall, drainage of the soil continues until maximum retention is reached; this is known as the field capacity. Uptake of the water by plants through their roots can reduce soil moisture to a value less than the field capacity, thereby creating a soil moisture deficit. The soil moisture deficit represents the millimetres of rainfall that would be required to bring soil water conditions back to field capacity. When plants are no longer able to extract further soil moisture, they have reached the "wilting point".

The water in the intermediate zone is free to drain downwards under the force of gravity. This water may either go downwards and recharge the groundwater (i.e., percolation) or move laterally in the unsaturated zone (i.e., interflow). Interflow may ultimately be discharged at surface streams. This is actually the main way in which rainwater reaches streams and rivers in areas where the rocks themselves are not

very permeable but are overlain by permeable soil. The concept of permeability will be explored in more detail in Chapter 2.

Capillary water, where water is stored as a film surrounding rock particles, occurs due to the force between water molecules known as surface tension. This creates a process known as capillarity, which allows retention of water in the capillary fringe (see Fig. 1.4) and is fundamental to groundwater flow. The thickness of the capillary fringe varies depending on its material characteristics. For example, capillary rise is highest in rocks with finer pores (e.g., silt and clay, see Fig. 1.5). It is important to note that the capillary fringe zone may be saturated, but water is held there

Figure 1.4   In the capillary fringe, the pores are mostly filled by air and the capillary water is adhered to rock particles. In the saturated (phreatic) zone, the pores are completely filled with water
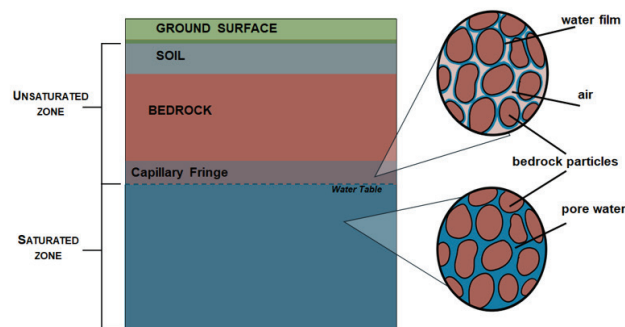
Figure 1.5   Relative capillary rise in four common soil types.
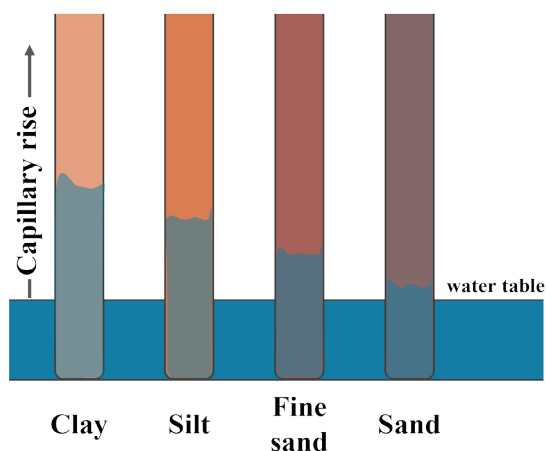
by capillarity. In the saturated zone, water is at a pressure higher than the atmospheric pressure, and the water table represents the point at which the water pressure is at atmospheric pressure.

There is always a thin film of water around rock and soil particles and capillary water can never be removed from an aquifer. This has direct implications, for example, for evaluating the amount of water which can be extracted from groundwater. The yield will be overestimated if it is calculated purely on the basis that all the voids are filled with water and all such water is obtainable. Actual yield, known as specific yield, is less than the yield that can be derived from void space alone. The specific yield can be found from the ratio of water which would drain away naturally from rock compared with the actual volume of water it contains. Specific retention is the term used to describe the proportion of water locked in the rock due to surface tension. Specific retention values are likely to be lower in rocks with larger pores because relatively large pores retain only a thin film of water after draining, while rocks with very fine pores (i.e., chalk) retain almost 100 per cent.

1.3 Groundwater inputs and outputs

1.3.1 Infiltration

One of the main inputs to groundwater comes from the absorption of surface water into the soil (i.e., infiltration), which is transported downwards by percolation. There are a number of factors which determine how much water contributes to infiltration compared with surface runoff, or is otherwise removed (e.g., by evapotranspiration). These are:

Gradient of the ground. Steeper ground will encourage greater runoff because surface water flow velocity is greater, giving less time for infiltration to occur.

Specific properties of the ground surface. The relative ease with which water might infiltrate, for example into sand compared with concrete.

Vegetation (or other) surface cover. Some types of surface cover prevent infiltration whilst others

encourage it. Certain types of vegetation may decrease runoff rates, because plant roots can create small flow pathways into the ground encouraging and increasing infiltration compared with non-vegetated surfaces. Conversely, less rainfall may reach the ground because it may be intercepted by plant leaves. Some rainfall may still reach the ground indirectly by leaf-drip, and some may be used directly in transpiration and be returned to the atmosphere.

Rainfall intensity. The more intense the rainfall, the more likely it is to cause small-scale compaction of the surface, reducing infiltration. If less water soaks into the ground as a result, it is more likely to become runoff. This is why tropical regions, which commonly experience high intensity rainfall, have a higher percentage of surface runoff compared with temperate climates, where rainstorms are less intense.

Duration of precipitation and degree of ground saturation. If the upper soil layer reaches infiltration capacity, which refers to the maximum rate at which infiltration can occur for a particular medium, then the surplus water that cannot be infiltrated will runoff from the surface as overland flow (Box 1.2).

In addition to these locally specific factors, infiltration rates can change over time; i.e., decrease as dry pore spaces between soil particles fill with water and become stable following soil saturation. This makes it even more difficult to predict the proportion of water that enters groundwater compared with the amount which runs off on the Earth's surface. Moreover, some of the water that infiltrates can be drawn back to the surface by negative pore pressure (also known as capillary action). This occurs essentially because there is a deficit of water in the atmosphere. It can be measured locally with the help of a tensiometer. This phenomenon explains why salt pans or salt flats occur in some arid regions, where water evaporates leaving its minerals to accumulate on the surface.

Plants can also return some of the infiltrated water back to the surface. A mature oak tree, for example, can draw water from as much as 10 m deep into the ground. In this case, and if the local water table is shallow, it is possible for water to be lost even from the saturated zone. Water from this process is then transpired into the atmosphere by the plant's leaves.

BOX 3.1 OVERLAND FLOW

When infiltration capacity is exceeded, either due to elevated intensity and/or duration of rainfall, or the condition and moisture content of the soil, water will begin to pond on the surface. Given even a small gradient, this ponded water will tend to flow down slope, which is the process known as overland flow (see Fig. 1.A).

Overland flow refers to the water that fails to infiltrate and travels over the ground surface towards a surface water body (e.g., a channel). There are two main types of overland flow:
- *Infiltration-excess overland flow* where rainfall intensity exceeds the infiltration capacity of previously dry soil.
- *Saturation-excess overland flow* where runoff caused by rain falling into saturated areas cannot infiltrate.

Figure 1.5 Cross-sectional view of overland flow, interflow and groundwater flow into a river channel
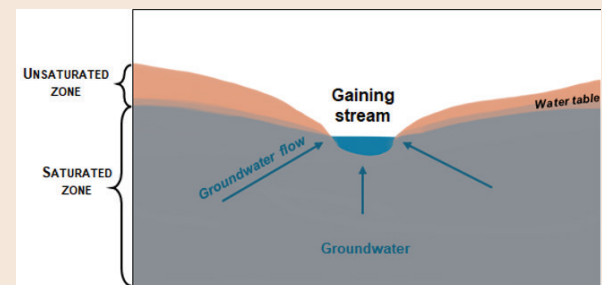
In order to predict local runoff and infiltration, all of these variables that are relevant in a particular area must be known.

1.3.2 Gaining and losing streams

In a topographic situation where a river bed (i.e., the channel in which a river flows) lies at a lower altitude than the water table, groundwater may discharge into it. Such rivers are known as gaining streams and represent one of the biggest single losses of water from groundwaters (see Fig. 1.6). The contribution to the river flow arising from groundwater discharge is often the largest component of the river baseflow.

Baseflow includes all contributions to a streamflow that do not arise from surface runoff (e.g., input from standing water bodies, glacial meltwater and groundwater) (Bierman and Montgomery 2014). Rivers situated above the water table, represent the opposite scenario and water is discharged from the stream to groundwater. These are known as losing streams (Fig. 1.6). It is also important to note that, as well as interacting with surface water bodies, groundwater can also interact with other subsurface reservoirs, such as deep saline water bodies.

Figure 1.6 Gaining (top) and losing (bottom) streams
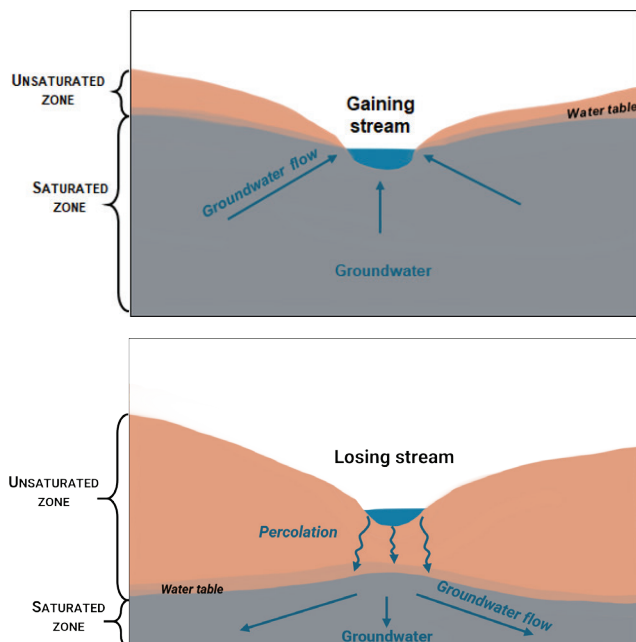
1.4 Groundwater balance

The amount of water that percolates downwards from the soil water into groundwater depends on the balance between evaporation, transpiration and rainfall. Solar energy is the driving force causing evaporation of water from surface water bodies and the soil. It also stimulates evaporation of water directly from plants (i.e. transpiration). The term evapotranspiration is then used to combine both phenomena. Potential evapotranspiration is defined as the amount of water that would evaporate or transpire from a surface if water was available to that surface in unlimited supply. In most situations, however, unlimited water supply is not available.

The change in groundwater storage (ΔS is a balance between groundwater recharge (R_N), stream flow loss to groundwater (Q_i), transpiration (T) and the groundwater loss to stream baseflow (Q_0). These are given in mm per unit time (e.g., millimetres of rainfall per day, per year, etc.) and with an area term they can be converted into discharge (m³/s).

$$\Delta S = R_N + Q_i - T - Q_0$$

Assuming that no artificial recharge or abstraction of groundwater is taking place, over a period of time the change in groundwater storage (ΔS) would be equal to zero, and the groundwater table level would remain stable:

$$R_N + Q_i = T + Q_0$$

This equation can help in determining whether artificial abstraction and recharge are sustainable and whether they will lead to significant changes in the water table level. In the following example, abstraction by pumping (Q_p) has been included in the water balance equation:

$$\Delta S = R_N + Q_i - T - Q_0 - Q_p$$

Assuming that all other parameters remain the same, the change in storage (ΔS) as a result of pumping will be negative, leading to a decline in groundwater level. This can then cause other serious consequences, for example, the baseflow component of a gaining stream may be lost, leaving it as an intermittent or ephemeral stream (Box 1.3). A reduction in groundwater storage may also cause, in more serious and rare cases, land subsidence (i.e., the sinking of the ground surface). Moreover, if over-abstraction occurs and groundwater levels continue to decline over time, this might have a negative effect on groundwater quality and availability. With careful management, however, it is possible to achieve a new steady state while pumping water from the system without leading to serious adverse outcomes.

Change in groundwater storage can be estimated from changes in groundwater levels in wells, provided that the storage properties (e.g., specific yield) are known. The volume of water lost from storage is simply the specific yield multiplied by the volume of rock drained. Specific yields are best determined using pumping tests (see Chapter 2). Alternatively, they

BOX 1.3 STREAM TYPES

Perennial streams are typically gaining streams and have water flowing all year round.

Intermittent streams are seasonal streams. These are generally losing streams, but groundwater provides enough water for a baseflow during certain times of the year (i.e., wet periods), with runoff and/or precipitation supplementing the streamflow. Larger seasonal streams are more common in dry areas.
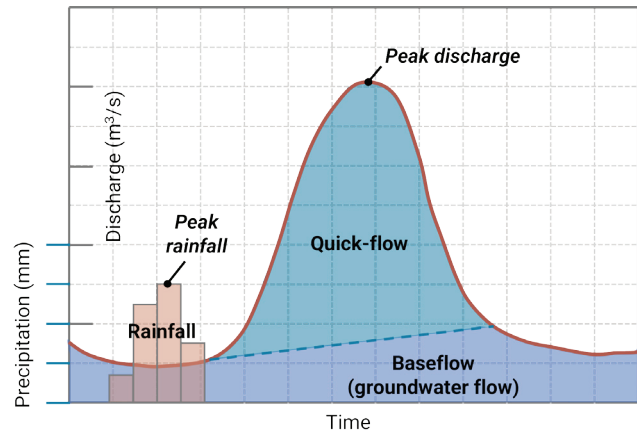
Ephemeral streams are precipitation-dependent streams. These are also classified as losing streams, with runoff and precipitation as primary sources of streamflow. Like seasonal streams, they can be found anywhere but are most prevalent in drier regions.

Figure 1.7 Hydrograph showing the quick-flow and baseflow components of stream flow following a rainfall event

can be estimated from the material properties of the saturated zone. It is important to note that in order to get a representative dataset, a grid of wells is needed across the region of interest.

Transpiration is one of the most difficult parameters to estimate, because it depends on many factors. It is commonly calculated through complex equations, which account for variables such as temperature, sunshine, wind, humidity, variations in soil type and the crops being grown. For detailed studies, it is possible to measure evaporation and transpiration locally by measuring soil moisture throughout the year. This is done using devices such neutron probes (Chanasyk and Naeth 1996). Alternatively, there are geochemical methods for estimating the proportion of precipitation that evaporates and the amount that contributes to recharge (e.g., Gaye and Edmunds 1996).

Estimating the proportion of water that enters the channel network quickly, rather than entering groundwater first, is normally done using a technique known as stream hydrograph analysis. A hydrograph is a plot of stream flow against time (see Fig. 1.7) and its analysis tends to recognise two main components: (i) the quick-flow derived from runoff, rapid interflow through the soil, and rain that falls directly into channels, and (ii) the baseflow, which consists of groundwater

discharge. Between rainfall events, streamflow represents mainly baseflow from groundwater. However, following a rainfall event, streamflow can rise rapidly as a result of quick-flow. Hydrograph separation into baseflow and quick-flow components is inevitably somewhat subjective, but it still provides a valid method for estimating both components.

1.5 Summary

- Groundwater is an important resource globally that is increasingly under threat from human activities

- Groundwater can provide vital supply sources where surface water is scarce, seasonal or absent, or already polluted, and is an increasingly important buffer against drought.

- The lack of groundwater monitoring in many countries means that the deterioration in groundwater quality is largely unknown at global scale

- Groundwater is recharged from rainfall by infiltration and percolation from the land surface and from surface water bodies. It contributes to baseflow in rivers and streams.

- The interconnection between surface and groundwaters means that poor groundwater quality can seriously affect surface waters and vice versa.

CHAPTER 2

AQUIFERS

2.1 Introduction

Groundwater (i.e., water stored in the saturated zones) can act as a natural reservoir, providing extensive and widely distributed water supplies. This is due to two intrinsic characteristics found in most groundwater environments: (i) large storage capacity, and (ii) slow rates of water flow. It is important to note, however, that not all rock layers (i.e., strata) store water in the same way. The following are some important terms and definitions used to describe the different types of water-bearing strata (Fig. 2.1):

Figure 2.1   Cross section showing different groundwater-bearing strata
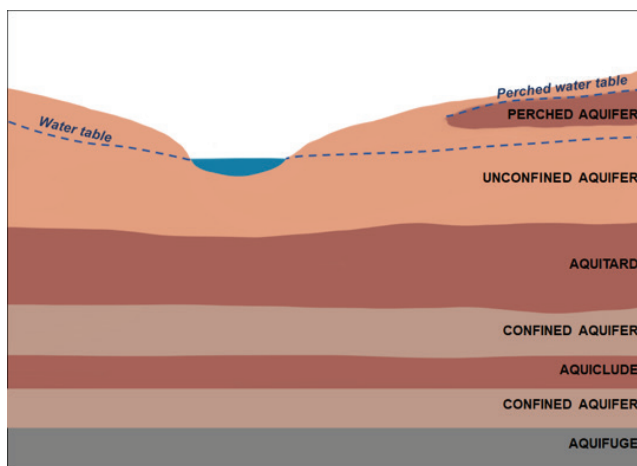
Aquifer. Geological strata which contain water and allow the movement of water within them. In order to permit water flow, the materials in them are expected to be both porous and permeable (Box 2.1) (i.e., sandstone). A well drilled into these strata would keep on re-filling as water is extracted.

Aquifuge. Geological strata below the water table which do not contain water. These strata are expected to have zero porosity and permeability (i.e., rocks with crystalline textures such as igneous and metamorphic rocks). Aquifuges are extremely rare because water is likely to be contained within fracture spaces.

Aquitard. Geological formation which contains water and is situated within the saturated zone, but has moderate permeability (i.e., siltstone). Such strata would be transitional between an aquifer and an aquiclude.

Aquiclude. Geological formation which contains water and is situated within the saturated zone but has low permeability. Here, porosity may be high, but water movement is restricted by the low permeability (i.e., claystone). A well drilled into these strata could take months to re-fill after water is extracted.

Unconfined Aquifers. Aquifers where the upper water surface (i.e., water table) is at atmospheric pressure and can rise and fall. These are usually closer to the ground surface than confined aquifers, and are quickly impacted by drought conditions.

Confined Aquifers. Aquifers confined by layers of low permeability both above and below. The confinement causes the water in these aquifers to be under pressure so that when they are penetrated by a well, the water rises inside the well. The level to which the water rises is called the potentiometric surface.

Perched Aquifers. Aquifers that are "perched on" (i.e., sit above) the local water table, in the unsaturated (vadose) zone. If saturated rock overlies relatively low permeability strata (e.g., aquitards), a locally elevated water table (known as a perched water table) can develop, creating a perched aquifer. These are variable (i.e., temporary) aquifers and do not provide reliable, long-term water supply sources, and can also

cause problems of slope stability. Perched aquifers may be of limited lateral extent, and only exist in response to particularly high infiltration periods, such as following a prolonged and heavy rainstorm. More rarely they may be of considerable lateral extent and thickness and are therefore occasionally mistaken for permanent aquifers.

From the above definitions, it is clear that some strata are conducive to groundwater storage and movement, while others are not. Strata of low permeability, such as aquifuges and aquicludes, are referred to as "confining layers", and their presence or absence determines how to best abstract water from an aquifer (see Box 2.2).

BOX 2.2 GROUNDWATER EXTRACTION POINTS AT DIFFERENT STRATA

Examples of the result of drilling wells to extract water from different rock strata can be illustrated with this hypothetical example.

Water extraction at point A. If a well is drilled at point A into the sandstone aquifer, which is overlain by a confining layer (i.e., a low permeability shale), water would rise to the potentiometric level (i.e., an imaginary surface determined by the pressure in the confined aquifer). Because the potentiometric level at A is above the ground surface, water from this well would overflow and this borehole could be described as an artesian well.

Figure 2.A **Three hypothetical groundwater extraction scenarios using three different boreholes (A, B and C) in different rock strata**
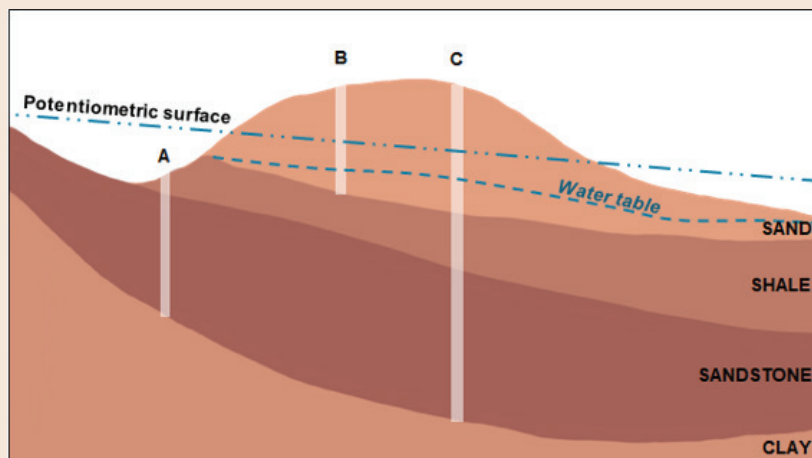
Water extraction at point B: If a well is drilled at point B, the water would only rise as far as the water table in the sand layer and not to the potentiometric level.

Water extraction at point C. This part of the sandstone aquifer is confined by the overlying shale. Hence, if a well is drilled at point C, the water would rise to the potentiometric level, as for point A. However, this level is below the ground surface at C and so this well would be described as a sub-artesian well.

Pumping water at B would not have any effect on water levels in boreholes A and C because these are fed from the underlying (confined) sandstone aquifer and not the sand. It is important to understand details like these if the objective of drilling the well is to lower the water table, for example, before excavating the ground.

2.2 Aquifers by rock type

2.2.1 Sedimentary rock aquifers

Most of the best aquifers around the world are found in sediments and sedimentary rocks (e.g., sandstone). Sedimentary rocks are formed from the deposition of particles or sediments derived from the weathering and erosion of other rocks. Sediments become consolidated and cemented during later diagenesis (i.e., processes that occur during conversion of sediment into sedimentary rock). This usually reduces porosity. However, subsequent fracturing and weathering may increase their porosity and permeability over time. The sedimentary rocks that make the best aquifers are usually the least cemented, but most sandstones and conglomerates will yield some water.

Limestone rock is highly soluble in rainwater leading to solution cavities and dissolution along joints, resulting in fissure flow permeability. Connectivity between such fissures and cavities is critical in determining yield, but it is difficult to predict whether a borehole sunk at random will intercept these. Also, because the cavities in limestone are relatively large, the rock tends to drain quickly after rainfall, making it an unreliable water source. Chalk is a type of limestone with closely-spaced cavities (it does not usually contain caves) which can result in a very good yielding aquifer, although more susceptible to drought than sandstone aquifers for the reasons just given.

2.2.2 Igneous and metamorphic rock aquifers

Igneous and metamorphic rocks are usually poor aquifers. This is largely because of the mode of formation of these broad rock groups. Igneous rocks are formed from the solidification of magma, a process which usually creates a texture of interlocking crystals. This normally produces very little primary porosity and low permeability. However, there are exceptions such as vesicular rocks, which are pitted with many cavities (vesicles), and basalt, both of which have a well-developed fracture network formed during cooling, resulting in high permeability. An example of the latter is the Columbia Plateau Basalts in the USA, which are one of the highest yielding

aquifers in the world (Price 1996). Other extrusive igneous rocks, such as pumice, may also have very high porosities, but their permeability is low due to poor connectivity between void spaces.

Metamorphic rocks are formed by the application of heat and/or pressure to existing rocks. This tends to reduce their porosity and permeability below that of the parent rock. However, secondary porosity may develop later (as in some igneous rocks) due to alteration and decomposition of minerals during weathering, or due to tectonic activity and stress release processes. Ultimately these can lead to fracture permeability. Metamorphic rocks usually develop into local small-scale aquifers which can be vitally important in areas where supplies of water are limited (Wright 1992).

2.2.3 Sand and gravel aquifers

On a global scale, about 90 per cent of developed aquifers are in unconsolidated materials, which comprise predominantly sands and gravels (Todd and Mays 1980). These can occur in river valleys and floodplains, buried or abandoned valleys, and intermontane valleys. The high permeability commonly found adjacent to water courses gives very high aquifer yields, and this is often increased further from streams where groundwater contours permit (i.e., losing streams). Floodplains can also provide high yielding aquifers, but they are more variable and can be thin. In the western regions of the USA, intermontane valleys are used widely as aquifers (USGS 2016). They comprise deep valley deposits derived from erosion of adjacent rock walls and can be very productive. Groundwater into such aquifers is replenished from streams seeping into alluvial fans at the mouth of the valley. Another example is the unconsolidated fluvial deposits in Scotland where extraction is replenished quickly by seepage from nearby rivers (Ó Dochartaigh *et al*. 2015). These aquifers are basically used as natural water filters.

2.2.4 Clay aquifers

Both sand and clay deposits are quite porous but, while sand and sandstone can be quite permeable, clay and mudstone are not. Despite having high porosity, they are composed of very fine pores,

which causes the surface tension to be so high that permeability is low. As a result of this, clays are very poor aquifers.

2.3 Aquifer properties

2.3.1 Porosity

As defined in Box 2.1, porosity is a parameter that describes the volume of void space within a material as a percentage of the total volume of that material. Porosity can vary from near zero in dense rocks to more than 60 per cent in loosely consolidated deposits (Domenico and Schwartz 1998). It is usually denoted as α, ϕ or n, and in this guidebook it will be referred to as n (see below):

$$n = \frac{V_v}{V_v + V_s} \times 100 \tag{1}$$

Where:

n is the porosity (%)
V_v is the volume of voids, and
V_s is the volume of solids in the material.

Another term which is sometimes used to represent porosity (and is especially used in civil engineering) is the void ratio, e. This is expressed as:

$$e = \frac{V_v}{V_s} \tag{2}$$

The void ratio can be expressed as a function of porosity, and vice versa:

$$e = \frac{n}{1 - n} \quad and \quad n = \frac{e}{1 + e} \tag{3}$$

Porosity can be further classified as primary and secondary. The original void space created during genesis rock formation is referred to as primary porosity and usually represents voids in the interstitial spaces between or within grains. Secondary porosity is used to describe voids, fractures or cavities generated after a rock has been formed and results from processes such as weathering, erosion, diagenesis and tectonic activity. Examples of the ranges of porosity for different sediments and rock types are given in Table 2.1.

Table 2.1   Porosity values for different sediments and rock types

Unconsolidated sediments	Porosity (%)	Consolidated rocks	Porosity (%)
Gravel	25−35	Sandstone	5−30
Sand	25−45	Limestone and dolomite	1−20
Silt	35−50	Karst limestone	5−30
Clay	45−55	Shale	1−10
Sand and gravel	20−30	Vesicular basalt	10−40
Glacial till	20−30	Fractured basalt	5−30
		Tuff	10−60
		Fresh granite and gneiss	0.01−2
		Weathered granite and gneiss	1−15

Source: Data from Chilton (1996)

Material properties affecting primary porosity

The primary porosity of a rock is closely related to its textural properties (such as grain shape and degree of sorting), the rock fabric (e.g., packing), and the rock's diagenetic and weathering history. These influence sorting, cementation and mineral re-deposition. The way in which these properties influence porosity are described below.

Grain Shape. Angular grains tend to interlock more than rounded grains, and greater interlocking usually gives rise to lower porosity.

Grain Size. Geometrical grain size should have no effect on porosity. However, small grains are often more angular or platy (e.g., clay minerals) which leads to higher porosity as seen above.

Degree of Grain Sorting. The extent to which grains are sorted influences porosity. The more uniform the grain size, the more space that will be retained between grains, which results in higher porosity. Conversely, in a poorly sorted material characterised by a wide range of grain sizes, finer grains can fill the spaces left between the coarser grains, leading to lower porosity. Note that the definition of sorting used here is that commonly used by geologists. Engineers tend to use the term "well graded" to mean a wide range of grain sizes.

Packing. This describes the way grains fit together. If there is good packing between grains this means that little space is left between them and, consequently, the porosity is low.

Cementation. Cementation describes the accumulation of binding (e.g., cementing or detrital) materials around grains that fills the voids. Rocks are usually less porous than their uncemented (i.e., un-lithified) counterparts.

Geological and geochemical processes affecting secondary porosity

Secondary porosity may develop due to geological and/or geochemical processes that can occur after rock formation. The amount of secondary porosity depends on a wide range of factors including:

(i) rock mass structure (e.g., fracture spacing and arrangement), (ii) lithological history (e.g., sedimentary structures, deformation), and (iii) diagenetic, weathering and erosional history (e.g., fracture infilling, healing and coating, rebound fracturing). The effects of diagenesis, weathering, and some miscellaneous fracture-causing processes are described below.

Diagenesis. Sediments may be subject to diagenetic processes during and following burial. This may involve chemical reactions between mineral grains and migrating pore fluids and can result in either increased or reduced porosity. Burial usually results in compaction of unconsolidated sediments, and this is achieved by the re-arrangement or even the deformation of grains (increasing packing, for example) and the expulsion of pore fluids. In chalks, where cement contact between grains occurs very early in the burial process, porosity is usually very high (commonly between 20 per cent and 40 per cent). This happens because early cementation makes the material rigid, and relatively resistant to compaction. As a result, much of the inherent porosity of the sediment is retained. However, at later stages in diagenesis, dissolution processes may still enhance porosity within the inter-granular cementing material.

Weathering. Weathering is defined as the chemical decomposition and alteration of rock constituents. More commonly, dissolution of soluble rocks may lead to the enlargement of pores, fractures or cavities within the rock, increasing porosity. This is most common with limestones but can also occur when igneous and metamorphic rocks are subject to weathering.

Miscellaneous fracture-producing processes. Although fracture porosity accounts for a very small percentage of total sediment porosity, aquifers are often so large that it results in significant storage volumes for groundwater. This porosity is mostly created by mechanical and lithological discontinuities introduced into a rock mass by external factors such as tectonic activity (e.g., joints), stress relief (e.g., rebound fractures), dissolution of cavities in soluble rocks (e.g., limestone), lithological variations (e.g., bedding planes), and human activities (e.g., blast-induced fracturing around tunnels).

Effective and total porosity

A distinction should be made between effective and total porosity. Total porosity refers to the total amount of void space within the rock, while effective porosity refers only to the amount of void space that can store and supply water. This distinction is made because some pores may be: (i) completely isolated, (ii) too fine to absorb water, or (iii) surrounded by smaller pores and effectively trapped (i.e., "trapped pores"). Consequently, some pores will not contribute to the void space which stores and supplies water within a material.

2.3.2 Permeability

As defined in Box 2.1, permeability describes the ease with which a fluid can pass through a material. This fluid can be air, water, or some other gas or liquid. Permeability is mainly controlled by three key rock features: (i) pore size distribution, (ii) connectivity between pores, and (iii) characteristics of the fracture network. Rocks which do not easily allow water movement through them are said to be impermeable. Permeability is a direct reflection of the connectivity between voids in a rock mass, and the size of these connections is particularly important in determining the ease of groundwater movement.

Flow through porous rocks can be predicted by Darcy's Law which states that the discharge (i.e., rate of flow) is equal to the product of the hydraulic conductivity, the cross-sectional area, and the hydraulic gradient:

$$Q = K \times A \times i \qquad (4)$$

Where:

Discharge is Q (m^3 d^{-1})
Hydraulic conductivity is K (m d^{-1}) or (m per day)
Cross sectional area is A (m^2)
Hydraulic gradient is i (−)

It can be extended to describe flow in fractured rocks, provided certain conditions are met. These are: (i) that the volume of rock tested contains a large number of fractures, and (ii) that the fractures are narrow enough to prevent turbulent flow. Essentially, blocks of rock separated by fractures can be thought of as if they were grains. The approach to predicting the flow in fractured rocks using Darcy's Law is applied to the entire rock mass (i.e., the rock and its fractures) and is called the continuum approach. For this to work, the permeability for a block of rock large enough to contain a representative number of fractures must be known (either measured or estimated). It is also important to note that fracture systems may exist on several scales, and as such, fractured rocks may have different permeability values depending on the scale at which the measurement is made.

Hydraulic conductivity depends on two main factors: the porosity of the medium, and the properties of the fluid (e.g., viscosity and density). Typical hydraulic conductivities for some geological materials are given in Fig. 2.2. Hydraulic conductivity can, and most often does, vary within an aquifer. If K is the same at every location within a geological unit then the formation is described as homogeneous; however, if it varies from place to place within a geological unit it is described as heterogeneous. Geological units are also classified as being isotopic, indicating that the hydraulic conductivity is the same in all directions within a geological unit, or anisotropic if it varies according to a specific flow direction (i.e., horizontal or vertical).

The cross-sectional area of interest, A, can be calculated for an aquifer as the product of the

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Figure 2.2   Hydraulic conductivity of different geomaterials (adapted from Heath 1983)
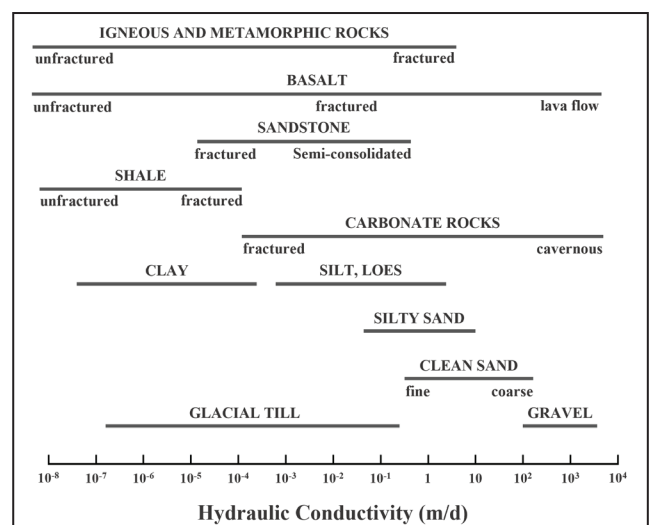
thickness of the saturated zone in metres, denoted as *b* and the width of the aquifer under consideration in metres, denoted as *w*:

$$A = b \times w \tag{5}$$

It is important to remember that the main area of interest is the saturated zone, because this is the zone likely to yield water in quantity. The actual cross-sectional area of the aquifer is perpendicular to the direction of flow.

Substituting for A in equation (4), discharge then becomes:

$$Q = K \times b \times w \times i \tag{6}$$

Transmissivity, *T*, given in $m^2\ d^{-1}$ describes how easily water can move through an aquifer and determines permeability. It is defined as the product of the hydraulic conductivity, *K*, and the saturated thickness of the aquifer, *b*. Thus, discharge can also be expressed as a function of transmissivity by substituting $K \times b$ with *T*:

$$Q = T \times w \times i \tag{7}$$

One reason hydrogeologists commonly use *T* rather than *K* to describe aquifers is that they often do not know the aquifer thickness (*b*). This is because in rock units such as Chalk, for example, most of the hydraulic conductivity is focussed in the upper few tens of metres, and it is difficult to say how thick the conductive zone really is. Also, in layered aquifers, all the layers have different hydraulic conductivities. Hydrogeologists get around this problem by measuring the transmissivity (*T*) *in situ* and then using it directly to make predictions about the amounts of groundwater that can be extracted. For these calculations it does not matter exactly where in the aquifer the water is flowing, i.e., whether it is mainly in one highly permeable bed or is more widely distributed.

Obtaining hydraulic conductivity and transmissivity values

There are three general approaches to finding the value for an aquifer's hydraulic conductivity, *K*. The first two options are to perform laboratory testing or to estimate it based on other aquifer properties, such as grain size and porosity (for matrix flow aquifers)

or fracture properties (for fractured rock aquifers). However, the more accurate method is field testing (e.g., pumping tests). In all these cases, transmissivity (*T*) can then be obtained by multiplying (*K*) by the aquifer thickness (*b*). The thickness of the aquifer can be obtained from borehole data, geophysical methods (these are less accurate), or from geological maps, although the latter should be used only as a last resort. For further information on these approaches, see Delleur (2016).

2.4   Groundwater flow

Groundwater flow is defined as the flow of water that occurs in the saturated (phreatic) zone, where aquifers are located. Under conditions of low permeability, such as in clay and silt aquifers, very slow velocities occur (mm per year), whereas coarser grained formations (such as sandstones, etc.) can have velocities up to several metres per day. The fastest flow velocities are found in fissured formations like Chalk, with velocities up to several kilometres per day possible where there is conduit flow. Compared with surface water, therefore, most groundwaters flow very slowly and have long residence times (Fig. 2.3). Consequently, if an aquifer becomes contaminated, it may be months, years, or even decades, before the contaminant is eliminated naturally. Understanding the direction of flow helps in planning where monitoring is needed and in anticipating where contaminants may move between groundwater and surface water.

Figure 2.3   Different residence times for groundwaters compared with surface waters
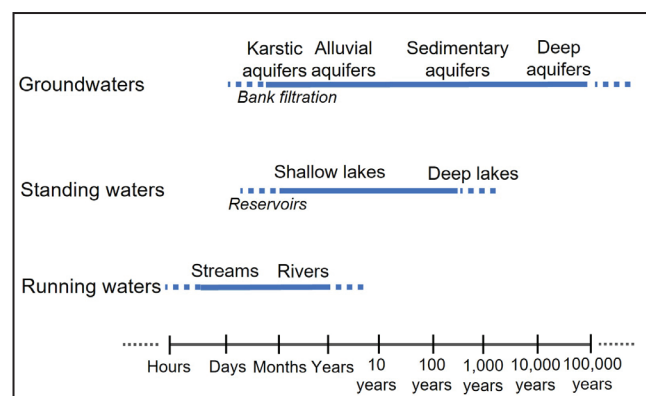
Aquifers can be confined or unconfined and their different properties result in different groundwater flow conditions. In unconfined aquifers, for example, the water table is often used as an important local parameter in groundwater flow calculations, whilst in confined aquifers potentiometric surfaces are used. It is also important to recognise that certain assumptions and simplifications are made in order to calculate the rate of groundwater flow, which may not necessarily align with the real aquifer conditions. These must be well understood and considered when interpreting results.

Differences in pressure and elevation, which are created by differences in water level leading to hydraulic gradient, can be sufficient to cause movement of water, including movement uphill. In other words, either elevation or pressure (or a combination of both) can create a potential difference which allows water to flow. Water flows from regions of high potential energy (high elevation or pressure) to regions of low potential energy, and this potential energy reduces as the water flows through an aquifer. This potential for fluid to flow through porous media is known as the *fluid potential* and has units of energy per unit mass of fluid.

Hydraulic head, h, also known as total pressure or total head, is the level to which water rises above a reference plane (datum) in a borehole or tube, and reflects a combination of the elevation head (denoted as h_e or h_z) and the pressure head (denoted as h_p). The elevation head, h_e, represents the elevation of the point of interest relative to a reference plane, and pressure head, h_p, is the height of water above a point of measurement (that is the height of the water column, which can be measured using a piezometer).

Water always flows from points of high hydraulic head to points of low hydraulic head, as it always flows from high to low potential energy (Fig. 2.4). Comparison of the hydraulic head between two different points in a flow system can be used to determine whether flow is occurring, and in what direction, as well as the magnitude of the driving force.

The *hydraulic gradient*, is the change in pressure over a distance:

Figure 2.4   Schematic showing groundwater flow lines and flow direction due to difference in the local hydraulic head

$$e = \frac{\Delta h}{\Delta l}$$
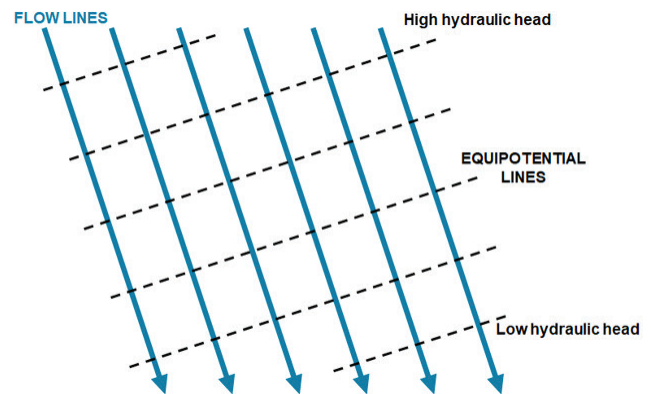
Where Δh is the difference in the height of the water tables between two points of interest in an unconfined aquifer, and Δl is the distance between these points. In the case of confined aquifers, Δh is the difference between the height of the potentiometric surfaces.

Water flows in response to a hydraulic gradient (i), and the direction of the hydraulic gradient dictates the direction of groundwater flow (Fig. 2.5).

Figure 2.5   Determination of direction of groundwater flow from the hydraulic gradient: example of horizontal (left) and vertical (right) hydraulic gradients

$$i_h = \frac{\Delta h}{\Delta l_h} = \frac{h_1 - h_3}{\Delta l_h}$$

$$i_v = \frac{\Delta h}{\Delta l_v} = \frac{h_1 - h_3}{\Delta l_v}$$
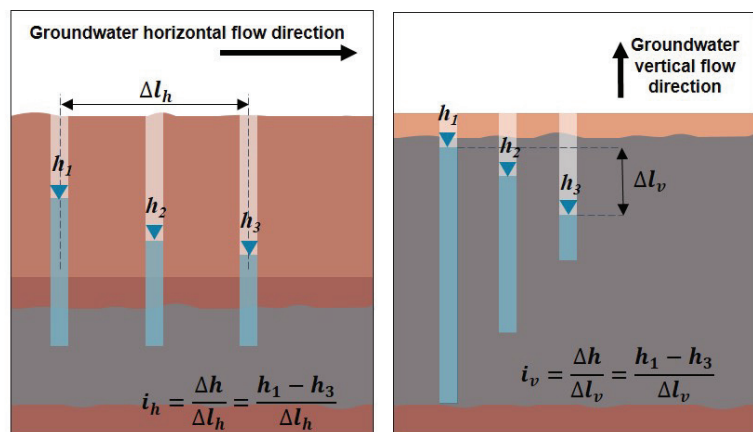
Specific yield is an aquifer property that determines the amount of water that can be removed from an unconfined aquifer. In practice, it is the amount of water that can be extracted per unit area (i.e., m^2) of unconfined aquifer which would cause the water table to drop by 1 m. Theoretically, the specific yield can also be defined as the ratio of water which would drain away naturally from a rock or soil compared with the actual volume of water contained by it (see Table 2.2). Due to surface tension and capillarity (see section 1.2) some water will always remain as a thin film between pore spaces. This is known as specific retention. Both specific yield, S$_y$, and specific retention, S$_r$, are expressed as volume per volume, and the sum of the two is equal to porosity (see section 2.3.1).

Storativity (or the storage coefficient) defines the volume of water that can be removed per unit area (i.e., m^2) of confined aquifer causing a hydraulic head reduction of 1 m, its value is highly dependent on the compressibility of the aquifer matrix; it is higher for uncemented aquifers. Storativity, S, is the equivalent to specific yield, S$_y$, for confined aquifers — both represent the amount of water that can be extracted by reducing the hydraulic head. Storativity values are usually much smaller than specific yields due to differences in the physical process occurring in confined and unconfined aquifers after water is removed.

When the hydraulic head is reduced in a confined aquifer, despite obtaining a yield, the column from which the water was extracted is still full of water, meaning that the pore spaces have not actually been drained. This is not the case in unconfined aquifers. The reason for this is that the water column contracts due to the reduction in pressure between pore spaces in the confined aquifer. This effect also occurs in unconfined aquifers, but it is ignored because the amount of water released is small compared with the amount of water draining from the pores.

Specific discharge, q, also known as volumetric flux, is defined as the volume passing per unit area per unit time through a porous media, and is expressed as follows:

$$e = \frac{Q}{A}$$

Where Q is the volume of fluid passing per unit time (i.e., through an aquifer), and A is the cross-sectional area. Substituting this into the formula for Darcy's Law (equation 4 in section 2.3.2), the specific discharge (m s^{-1}) can be described as:

$$q = Ki$$

Where K is the hydraulic conductivity and i is the hydraulic gradient.

Table 2.2   Specific yield values for different sediments and rock types

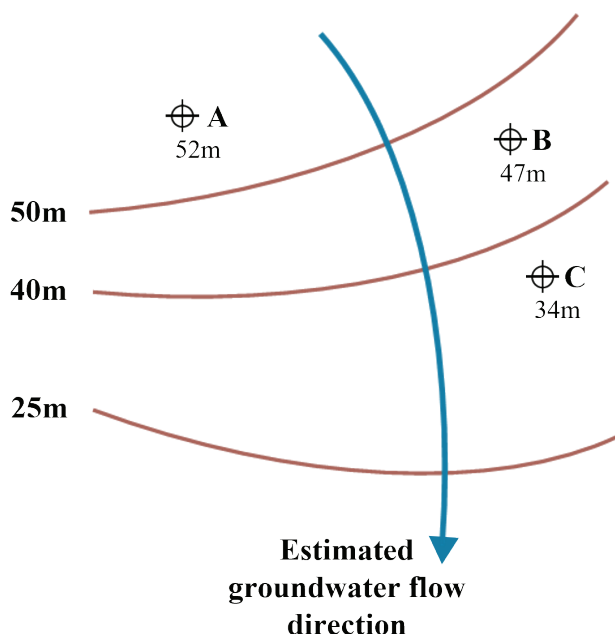| Unconsolidated sediments	Specific yield (%)	Consolidated rocks	Specific yield (%)
Gravel	15–30	Sandstone	3–15
Sand	10–30	Limestone and dolomite	0.5–10
Silt	5–10	Karst limestone	2–15
Clay	1–5	Shale	0.5–5
Sand and gravel	10–20	Vesicular basalt	5–15
Glacial till	5–15	Fractured basalt	2–10
		Tuff	5–20
		Fresh granite and gneiss	<0.1
		Weathered granite and gneiss	0.5–5

Source: Data from Chilton (1996)

2.4.1   Groundwater tracing

Groundwater flow into wells where natural conditions are considered can be measured using tracers. The principle of tracing is that a detectable substance that is added to the groundwater via a pre-drilled well can be detected elsewhere in the aquifer. This provides information on flow rate (velocity) and direction.

It is important to note that in order to perform a successful tracer study an approximate idea of groundwater flow direction must be previously known. For this, a key parameter is the local water level, which can be measured using a conductivity meter or other device. The water level in the borehole relates to topography and so it must be converted to Above Ordnance Datum (AOD) or some other datum to find flow direction. To do this, borehole top levels must be surveyed. Once the water level in several boreholes is known, a flow net can be drawn which would indicate flow direction. For an isotropic, homogeneous aquifer, the direction of groundwater flow will be at right angles to groundwater level contours (see Fig. 2.6).

Ideally, flow direction needs to be estimated on the basis of water level in several boreholes. Boreholes

drilled especially for this purpose would be expensive, so existing boreholes are used wherever possible.

Once flow direction is estimated, the tracer study can be performed. Three key parameters recorded are: (i) the time of first appearance of the tracer in the downstream borehole, (ii) the time it takes for the tracer to reach peak concentration in the downstream borehole, and (iii) the time it takes for the tracer to become undetectable again. The concentration versus time plot for the receiving borehole is sometimes called a "breakthrough curve" (Field 2020). However, it is important to note that the actual tracer flow paths are more complex due to tortuosity where particles take a convoluted pathway through different pores and the pathway is not linear (see Fig. 2.7). In a fractured aquifer, a tracer will only migrate where the fracture networks are connected over large distances.

Figure 2.6   Estimated groundwater flow direction based on groundwater level contours determined from the boreholes, A, B, and C

Figure 2.7   The average linear flow path of water between bedrock particles compared with the actual water flow path
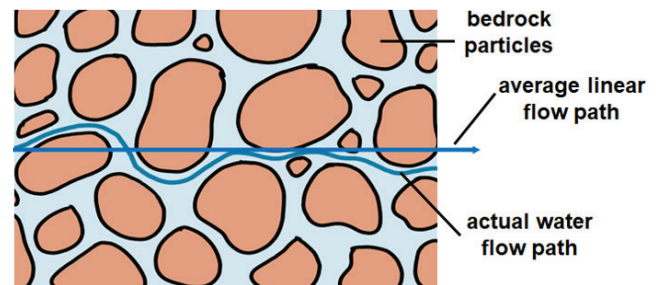
Types of tracers

An ideal tracer used in groundwater investigations must be dispersible, dilutable, detectable, and non-toxic and harmless. It also needs to last long enough in groundwater to be detected at the downstream borehole. Below are a few substances that can be used as tracers under different circumstances:

Fluorescent dyes. A variety of dyes have been used in the past in water tracing. Nowadays those that can be seen with the human eye are considered unacceptable and only fluorescent dyes are still used. These are detected with a fluorometer. To obtain direction and velocity of groundwater flow it is best to use a non-sorbing dye (i.e., a dye that does not attach to surfaces

either by absorption, adsorption, or a combination of the two). An example is a form of fluorescein called uranine, which is both cheap and non-toxic.

Optical brighteners. Optical brighteners are similar to dyes and can be detected with minimum technology (e.g., cotton wool and UV light). An example is Photein CU. It is important to note, however, that such compounds remain in the environment for a very long time.

Chloride and the other halogens. Common salt was one of the earliest tracers used in hydrogeology. Its main advantages are that it is cheap and easily detectable with a conductivity meter lowered down a borehole. However, in order to trace it, high quantities are needed to ensure no confusion with background levels of salt in the groundwater. This can cause problems if the water is to be used for consumption. To get around this issue halogens can be used, but these are more expensive and require more sophisticated detection methods. The halogen anion is usually chosen as a tracer because cations often undergo reactions (such as sorption) with aquifer materials.

Suspended particles. Suspended particles are used in conduit flow aquifers such as karstic limestone. They can range in size from small pieces of paper to fluorescent microspheres, bacterial spores and bacteriophages (a type of non-harmful virus). As they need to be held in suspension, they are useful for detecting turbulent (i.e. non-Darcian) flow conditions. Bacterial spores, bacteria and bacteriophages in particular, are also useful for mimicking the behaviour of pathogenic organisms in groundwater.

Gases. Dissolved, stable gases like helium are more recently used, non-toxic, non-reactive types of groundwater tracer. They have the advantages of not significantly affecting the density of the water and being detectable at very low levels using gas chromatography. However, care must be taken that these gases do not escape from the dissolved state when injecting and sampling.

Radioisotopes. The deliberate addition of radioisotopes to groundwater is limited due to public acceptability. However, radioisotopes entering from the atmosphere have been used as tracers in groundwater studies. Carbon-14 (^{14}C) and tritium (^{3}H) are known examples of these. Their use relies on the fact that the amount of decay (i.e., the decrease in the amount of radioisotope) from one point in the aquifer to another is indicative of travel time.

2.5 Summary

- Water stored in pores, fissures and fractures of rock formations forms natural groundwater reservoirs, known as aquifers

- Different rock types support varying amounts of water storage, depending on the porosity of the rocks and whether there are major fissures present.

- Groundwater flows very slowly, downgradient from recharge areas to discharge areas, depending on the grain size and presence of fissures in the saturated zone.

- Groundwater flow velocities may vary from mm per year to metres per day and thus it can take a very long time for contaminants to be flushed through an aquifer.

- Groundwater movement can be studied using tracers.

CHAPTER 3

GROUNDWATER QUALITY AND CONTAMINATION

3.1 Introduction

Understanding natural groundwater quality is essential for understanding whether contaminants are present and how they may behave in the groundwater. Natural groundwater quality at different locations can vary substantially and it is important to consider each aquifer in the context of its surroundings (i.e., the catchment characteristics such as geology and topography) and to interpret water quality information accordingly (UK Groundwater Forum n.d.). Activities such as mining, smelting (i.e., metal extraction from its ore), deposition of atmospheric emissions (e.g., from smelters and vehicles), agricultural use of fertilisers and pesticides, and livestock enclosures are generally non-point sources of groundwater contamination. Point sources are usually associated with industrial sites (current and disused), landfill sites (e.g., waste and sludge disposal areas), septic tanks and latrines. and certain types of commercial sites where spillages or leaks of potential contaminants may occur (e.g., service stations). Once a contaminant reaches the soil, it can spread through ground and surface waters. Contamination and some natural chemical constituents of groundwater can pose potential risks to human health, to the suitability of the water resource for human use and to the natural ecosystem. It is therefore essential to understand which substances may be harmful in groundwater and how they behave in the subsurface.

3.2 Physico-chemical characteristics

Some basic physico-chemical parameters are usually measured to aid in understanding the natural quality of the groundwater. These must be measured directly at the wellhead because their values may change in the samples after collection. These parameters include temperature, electrical conductivity, potential of hydrogen (pH), dissolved oxygen, and oxidation-reduction potential.

The temperature of groundwater generally remains within a narrow range regardless of seasons. Measuring groundwater temperature is important because it influences other groundwater parameters (electrical conductivity, pH, etc.) as well as chemical reactions in the subsurface. Moreover, more recently, groundwater temperature surveys have become a relevant method of geothermal energy identification because some shallow groundwaters can be used as heat sources for domestic heating/cooling.

Electrical conductivity (EC), also known as specific conductance, is the ability of water to conduct an electric current at a given temperature. It is measured in microSiemens per centimetre (μS cm^{-1}). Its value is a direct measurement of dissolved ionic species (total anions and cations) in a solution, and it therefore has a direct linear relationship with the Total Dissolved Solids (TDS). Electrical conductivity can be used as an indicator of water–rock contact time and catchment residence time. Typical electrical conductivity values in unpolluted groundwaters range from 500 to 1,000 μS cm^{-1}. An elevated EC (>1,000 μS cm^{-1}) can be a direct indication of contamination. However, it is important to note that some groundwaters may have naturally high EC, such as those in coastal areas or in some types of anoxic (i.e., reducing) aquifers, where redox reactions could be creating more dissolved ions.

Potential of Hydrogen (pH) is a parameter that expresses the acidity or alkalinity of a solution on a logarithmic scale, where 7 is neutral, lower values are more acid and higher values are more alkaline. This means that a solution of pH 5 has 10 times the acidity of pH 6 and 100 times the acidity of pH 7. Groundwater pH can be an important indicator of chemical changes due to contaminants.

Oxidation−reduction reactions, also referred to as redox reactions, are important chemical and biochemical reactions that takes place in groundwater. In simple terms, redox reactions primarily involve the transfer of electrons between two chemical species. The compound that loses an electron is said to be oxidized (the electron donor), and the one that gains an electron is said to be reduced (the electron acceptor). In groundwater, under natural conditions, redox reactions exert an important control on the distribution of elements and compounds like oxygen, nitrate (NO_3^-), iron (Fe) and sulphate (SO_4^{2-}). The oxidation−reduction potential measures the tendency of a chemical substance to oxidize/reduce another substance, including in groundwaters. It is measured in millivolts (mV) and can indicate possible contamination, particularly by metals, which could come from industrial waste.

3.3 Matter in groundwater

Matter comprises substances such as single elements and their combinations, and inorganic and organic compounds. Groundwater can contain matter in four distinct states: adsorbed, dissolved, colloidal and suspended. Knowing the state in which any particular compound normally occurs is helpful when planning how to detect them (i.e., in liquid, solid or combined forms) and where to sample because whether they are dissolved in water or solid particles will influence their transport within the groundwater.

Adsorption refers to the adhesion of atoms, molecules, or ions onto surface particles. Adsorbed matter binds to solid or liquid surfaces creating a film. Examples in groundwater are organic carbon and clay minerals. Matter is considered to be dissolved when it is incorporated into a gas or liquid to form a solution. Such substances can also be defined as the fraction

that cannot be removed by filtration (i.e., particle sizes smaller than 0.45 µm). They constitute the main state of matter in groundwater and include dissolved gases. Colloids are mixtures in which the dispersed particles are evenly distributed and do not settle in the dispersion medium, i.e., the groundwater. The particle sizes range from 1 to 500 nm (0.001 to 0.5 µm) and they may be filterable. An example is FeO(OH) as well as other transition metal hydroxides. A suspension is a mixture in which the particulate matter eventually settles in the medium. The particle size ranges from 500 to 1,000 nm (0.5 to 1 µm) and these particles can be retained by filtration (particle sizes are larger than 0.45 µm). Typical examples of suspended solids in groundwater are clay particles, organic matter, pathogens, stygofauna, etc.

Typically, the concentration of matter is measured in unit weight of matter per unit volume of medium (in this case the water). The unit used is g m^{-3} (grams per cubic metre) or g L^{-1} (grams per litre). Table 3.1 shows the range of notations that may be used for concentrations of matter in groundwater.

Table 3.1 Units of concentration of matter in groundwater

Dimensionless notation	Ratio	Concentration
Percent	1:100	% w/v
Parts-per-thousand	1:1000	‰ w/v
Parts-per-million	1:10^6	mg L^{-1}
Parts-per-billion	1:10^9	µg L^{-1}
Parts-per-trillion	1:10^{12}	ng L^{-1}

Dissolved solutes constitute the main state of matter in groundwater, and therefore it is important to understand their occurrence and typical concentrations. Table 3.2 shows which solutes typically occur at different concentration levels in groundwater.

Table 3.2   Typical concentration levels for different solutes in groundwater

	Concentration (mg L^{-1})	Concentration (µg L^{-1})	Concentration (ng L^{-1})
Major anions	HCO_3^-/CO_3^-, SO_4^{2-}, NO_3^-, Cl^-, SiO_2^{2-}	PO_4^{3-}, NO_2^-, F^-, Br^-, I^-, HS^-/ S^{2-}	
Major cations	Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+	H^+, NH_4^+, Fe^{2+}, Mn^{2+}, Al^{3+}, Ba^{2+}, Sr^{2+}, Zn^{2+}	
Gases	CO_2, O_2	CH_4, N_2O	
			Rare earth elements; noble gases; chlorofluorocarbons, etc.

Source: Freeze and Cherry (1979)

Major anions and cations account for 99 per cent of mineralisation in pristine groundwaters. When major ion analysis is performed, an anion-cation balance must also be carried out on the results of the analysis to ensure that the groundwater sample conforms to the principle of electroneutrality, i.e., that the sum of positive and negative charges within the water must balance to zero. If there is a significant deviation from electroneutrality there is a problem with the analyses. The deviation is determined as a percentage as follows:

$$\% \text{ Difference} = \frac{\sum cations - \sum anions}{\sum anions + \sum cations}$$

Where $\sum$ denotes the "sum of".

Values of 5 per cent or less for the difference are typical, and anything over 10 per cent is generally not acceptable.

Three major anions (i.e., HCO_3^-/CO_3^-, SO_4^{2-}, Cl^-) and four major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) are typically measured for this analysis. However, it is important to consider that large imbalances could be due to unmeasured anions (e.g., SiO_2^{2-}, NO_3^-) or cations (e.g., NH_4^+, Mn^{2+}/Fe^{2+}). In practice, the analytical results are often incorporated into a Piper diagram (Box 3.1) which aids in the interpretation of groundwater recharge sources, ion exchange and mixing along flow paths. For an example of the use of a Piper diagram see Dieng *et al.* (2017).

3.4 Chemical processes in groundwater

Different chemical processes occur at different depths due to the specific characteristics of that zone. In the unsaturated (vadose) zone, for example, the air-filled pores are open to the atmosphere. This allows leaching of minerals, gas exchange with the atmosphere and solute concentration in recharge waters to take place. Below the capillary fringe and water table (i.e., in the groundwater), a different set of chemical reactions may occur, due to water-rock interactions and reactions mediated by microbes (mostly bacteria). Some examples of these are mineral dissolution-precipitation, oxidation-reduction (redox) reactions, acid-base reactions, and gas production/ consumption.

Many chemical reactions occur in the saturated zone, from recharge to discharge within an aquifer system. Namely, acid-base reactions (solution/dissociation), redox reactions (biogeochemical transformation), solid phase interactions (solution-precipitation, surface phenomena), adsorption, and ion exchange (chemical evolution). A common sequence of physico-chemical processes from recharge to discharge along a flow path within a confined aquifer is shown in Fig. 3.1.

When precipitation infiltrates the soil in the recharge zone, the most important chemical change is the dissociation of carbon dioxide from the soil atmosphere. Here, soil organisms consume much of the oxygen that was dissolved during precipitation.

Figure 3.1   Chemical changes in groundwater from unconfined to confined conditions
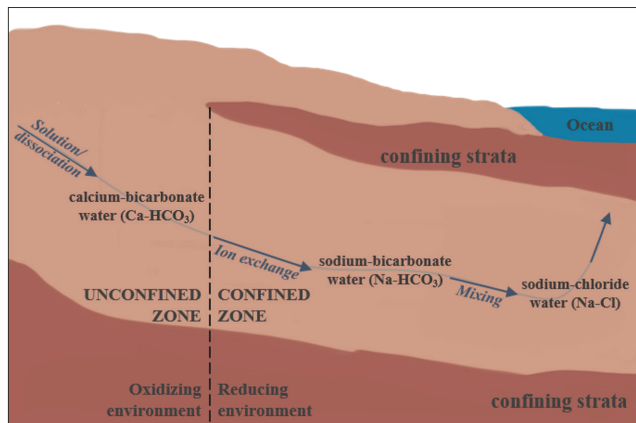
In other words, the carbon dioxide dissolves to yield hydrogen ions and bicarbonate ions. The solution is called carbonic acid. This is the first of several acid-base reactions:

$$H_2O + CO_2 = H^+ + HCO_3^-$$
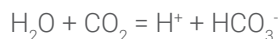
In the case of carbonate aquifers (and aquifers with carbonate cement), the next dominant reaction is the dissociation of calcium carbonate:

$$CaCO_3 = Ca^{2+} + CO_3^{2-}$$

Calcium carbonate does not readily dissociate in pure water, but the addition of ions H^+ from the production of carbonic acid greatly assists this process:

$$H^+ + Ca^{2+} + CO_3^{2-} = Ca^{2+} + HCO_3^-$$

What is evident already from (both acid-base reactions) is that the by-product of these first two chemical reactions is HCO_3^- (bicarbonate) and the resultant water type is calcium-bicarbonate (Ca-HCO$_3$). Bicarbonate is a very important anion and is often the dominant anion in groundwater chemistry. Its concentration is a useful indicator of the residence time of groundwater in an aquifer. Another important characteristic of the recharge zone is the presence of oxygen in the aquifer (derived from the atmosphere), which creates an oxidising environment.

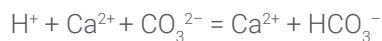As groundwater moves away from the recharge zone, two very important changes occur. The first is that the

geochemical environment changes from an oxidising to a reducing environment, and the second is that the predominant groundwater reaction is ion exchange. Ion exchange is the exchange of ions (in this case cations) between an insoluble solid and the solution that is in contact with the solid, i.e., the groundwater.

Most confined aquifers contain some clay minerals, which are common in fine-grained sedimentary aquifers. Clays are sheet-like minerals with active surfaces with a net negative charge. Because cations are positively charged, they are attracted to the clay

BOX 3.1 PIPER diagram

Piper diagrams (Fig. 3.A) are graphical representations of the chemistry in a groundwater sample. Cations and anions are plotted on separate ternary diagrams (i.e., triangles). The highest points in the cation plot are calcium (Ca^{2+}), magnesium (Mg^+) and sodium plus potassium ($Na^+ + K^+$), while in the anion plot these are sulphate (SO_4^{2-}), chloride (Cl^-) and carbonate plus hydrogen carbonate ($CO_3^{2-} + HCO_3$). These two plots are then projected into the summary diamond plot, known as the matrix transformation of ternary plots.

Figure 3.A   Piper diagram from the Saloum coastal aquifer. From Dieng *et al.* (2017) Licensed under CC BY-NC-ND 4.0
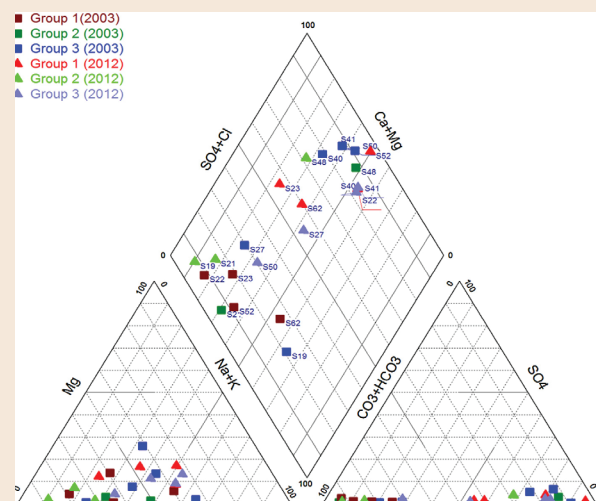
surfaces and become adsorbed. Ion exchange occurs when solution cations are exchanged for cations adsorbed on the surface of clay minerals, the resultant water type is then sodium-bicarbonate (Na-HCO$_3$).

As the groundwater flows deeper into the aquifer and closer to the coast, flow rates generally slow down (i.e., the hydraulic gradient is lower). This slower movement means longer residence time and greater opportunity for less soluble minerals to be dissolved. This results in an increasing dissolved content that is reflected in increased Total Dissolved Solids (TDS). At this stage, the dominant processes are redox transformation of HCO$_3^-$ and mixing, and the resultant water type is sodium-chloride (Na-Cl) as seen in Fig. 3.1.

3.5 Main threats to groundwater quality

There are many current threats to groundwater quality, mainly due to agricultural intensification, urbanisation, population growth and climate change. Some well-known consequences of these include aquifer salinization, and chemical (e.g., nitrate and pesticides) and microbial pollution. Contaminants can be broadly classified into four groups according to their composition:

Organic compounds: large molecules containing carbon, such as oils, petrol, coal tars, various solvents or treatment compounds, and food and animal wastes.

Inorganic compounds: heavy metals and their compounds, asbestos, ions in solution (such as ammonia, chloride, sulphate), and gases such as methane, carbon dioxide and hydrogen sulphide.

Radioactive compounds: such as uranium, radium, radon.

Pathogenic organisms: such as bacteria, viruses, protozoa.

In addition, naturally occurring contaminants can also have significant adverse impacts on the potential use of the water, notably arsenic and fluoride.

Groundwater contaminants can also be further categorised according to their state (i.e., colloidal, dissolved, non-aqueous phase liquid, gas) as described above. The state of a contaminant influences its mobility through groundwater and soil. For example, toxic metals present in mine waste cannot migrate through the subsurface unless in a dissolved state.

3.5.1 Microbiological contaminants

The issue of microbial contamination of groundwater supplies, particularly pathogenic microbes, is serious because it may lead to severe waterborne diseases. A recent review (Murphy *et al.* 2017), for example, presents clear epidemiological evidence of disease transmission due to groundwater contamination at a global scale, with an estimated 35.2 to 59.4 million cases of acute gastrointestinal infection attributable to groundwater consumption per year. These types of infectious diseases can result in widespread outbreaks amongst those using the same source of water. The disaster that occurred in Walkerton, Canada is a well-known example (Howard 2006) where over 2,000 people became ill and seven people died due to bacterial contamination of the municipal well water supply with *Escherichia coli* and *Campylobacter jejuni*. Pollution by pathogenic microbes is especially common in domestic wells that are poorly located, i.e., in close proximity to sources of faecal contamination such as septic tanks, latrines or livestock and are poorly constructed (Hynds *et al.* 2013). They can also enter groundwater through sewage overflows, sewage systems that are not working properly, and polluted stormwater runoff. Wells may be more vulnerable to such contamination after flooding, particularly if they are shallow, lack important protective features (e.g. a well-sealed cover) or have been submerged by flood water for long periods of time.

Pathogenic viruses (e.g., hepatitis, rotavirus), bacteria (e.g., *Escherichia coli*, *Salmonella typhi*, *Vibrio cholera*, *Campylobacter*), or protozoa (e.g., *Giardia*, *Cryptosporidium*) could all become potential groundwater contaminants. It is, however, difficult to detect all waterborne pathogens that may be present within groundwater resources. One key reason for this is that there are far too many different pathogens to

be monitored, which is why indicator organisms are often used in groundwater monitoring programmes. An example of an indicator organism is *E. coli*, which is an indicator of the presence of faecal material and, therefore, the possibility of faecally-transmitted pathogens. The indicator organism approach is based on the assumption that there is a quantifiable relationship between indicator density and potential health risks. For drinking waters, for example, a numerical standard of zero *Escherichia coli* per 100 ml of water is used to protect human health. Some examples of diseases and pathogens that can be transmitted by groundwater are:

Hepatitis A is a contagious liver disease that results from infection with the Hepatitis A virus. It can range in severity from a mild case lasting just a few weeks to a severe illness lasting several months. Hepatitis A is usually spread when a person ingests faecal matter from contact with objects, food, or water contaminated with the virus.

Cholera is an infectious disease that causes severe watery diarrhoea, which can lead to dehydration and even death if untreated. It is caused by eating food or drinking water contaminated with a bacterium called *Vibrio cholerae*. *Vibrio cholera* is usually found in food or water contaminated by faeces from a person with the infection. It is largely associated with lack of social development in the tropics (WHO 2021) where women and girls are tasked with water collection.

Campylobacter is a bacterium found in the intestines of many types of animals and is the most common bacterial cause of diarrhoeal illness. It is thought to be responsible for 5-14 per cent of all diarrhoea worldwide. *Campylobacter* infections have been found to be more prevalent during the summer months. Although a common cause of food poisoning, outbreaks have also been associated with contaminated water. An example is the outbreak in Havelock North, on the North Island of New Zealand (Gilpin *et al.* 2020).

Verotoxigenic *E. coli* (VTEC) are a specific group of *Escherichia coli*. Although most strains of *E. coli* are harmless and live in the intestines of healthy humans and animals, the VTEC strain produces a powerful toxin which can cause severe illness,

particularly in children under five and the elderly or immunocompromised. VTEC infections can occur through consuming contaminated food or water, or through contact with infected animals or surfaces. It can also be passed from person to person. Some studies have linked VTEC to the use of water from wells (e.g., O'Dwyer *et al.* 2017)

Cryptosporidium is a parasitic protozoan found throughout the world. It causes a diarrhoeal disease called Cryptosporidiosis. The *Cryptosporidium* parasite is transmitted via the faeces of infected people or animals. The parasite is protected by an outer shell that allows it to survive outside the body for long periods of time and makes it very resistant to chlorine-based disinfectants and high temperatures. Sources of *Cryptosporidium* to surface and groundwaters include seepage from livestock manure stores, runoff from livestock pens, direct contamination from grazing animals near watercourses, percolation of manure through soil and into drainage systems, and disposal of contaminated sewage into watercourses. Cryptosporidiosis outbreaks are usually associated with drinking water sources derived from contaminated surface waters, such as lakes and rivers, but evidence of *Cryptosporidium* in groundwater systems has been found (Stokdyk *et al.* 2019).

3.5.2 Nitrate

The main health concern associated with nitrate in drinking water is a condition in very young children known as methaemoglobinaemia, or blue baby syndrome. This occurs where nitrite (NO_2^-), a biproduct of nitrate (NO_3^-) reduction in the stomach, binds to haemoglobin in the blood, and in high concentrations hinders the uptake of oxygen. High nitrate concentrations in groundwater can result from diffuse agricultural sources, including organic and inorganic fertilisers, or point sources such as landfills, latrines and septic tanks (Fewtrell 2004). The WHO drinking water guideline value for nitrate (NO_3^-) is under 50 mg L^{-1}, or 11.3 mg L^{-1} as nitrogen (NO_3-N) (WHO 2017).

3.5.3 Salinization

Groundwater salinity can increase from a variety of processes, including (i) poor land drainage leading to waterlogging and the build-up of salts in the soils, (ii)

intrusion of sea water into aquifers in coastal areas caused by the over-abstraction from coastal aquifers, (iii) leaching of salts from soils in irrigation return flows (i.e., salinization of groundwater recharge), and (iv) the up-coning of saline waters from deeper aquifers resulting from intensive pumping of irrigation wells (Foster *et al.* 2018). A well-known example of aquifer overexploitation leading to problems of falling groundwater levels and increased salinities is the Rechna Doab aquifer in Pakistan, where shallow groundwater salinization occurred due to irrigation return-flow after over 100 years of inappropriate agriculture and irrigation practices (Foster *et al.* 2018).

3.5.4   Naturally occurring contaminants

There are several naturally occurring contaminants that can lead to serious health problems if present in high concentrations in groundwater supplies. Two examples are Arsenic (As) and Fluoride (F⁻). Arsenic (As) is a carcinogen which particularly affects the skin, lungs, kidney and bladder. It occurs in sulphide and arsenide minerals, in metal arsenites or arsenates and is absorbed as an accessory element on ferric oxides or oxyhydroxides. It is also mainly present in two dissolved ionic forms: arsenite ($As^{III}O_3^{3-}$) and arsenate ($As^VO_4^{3-}$). These have a complex geochemistry and can occur in groundwater in both reducing and oxidising conditions, at both low and high pH. Major deltas and alluvial plains composed of young sediments are particularly susceptible to groundwater arsenic problems. Arsenic has become a major health issue in recent decades, especially in parts of south and east Asia. In 2012 it was estimated that 60 million people were at risk from high arsenic levels in groundwater in this region, of whom about 40 million lived in Bangladesh and West Bengal (Flanagan *et al.* 2012). The Ganges delta of Western Bengal and Bangladesh is a rapidly accumulating sedimentary environment, where it is believed that arsenic is largely released by reductive dissolution of iron oxyhydroxides from young floodplain sediments.

Fluoride (F⁻) is an ion which may have beneficial effects for human health at concentrations between 0.5 and 1 mg L⁻¹ but can be very toxic at higher levels.

Concentrations above 1 mg L⁻¹ can give rise to mild forms of dental fluorosis. Skeletal fluorosis can occur at concentrations of 3–6 mg L⁻¹, and crippling skeletal fluorosis may develop when fluoride concentrations in drinking water exceed 10 mg L⁻¹ (WHO 2017). High fluoride concentrations in groundwater occur in many parts of the world, for example the rift valley of east Africa (Gaciri and Davies 1993). Fluoride is present in the mineral fluorite (CaF_2), and other common minerals of crystalline (including volcanic) and sedimentary rocks. High groundwater concentrations of these minerals are found in some volcanic rocks, and many granites and gneisses. However, high concentrations in groundwater can occur in other rock types and are often associated with hydrochemical 'maturity'. Calcium acts as a control on the solubility of the mineral fluorite. At high calcium concentrations, fluorite dissolution does not occur; thus, fluoride is normally associated with groundwaters where calcium concentrations are low.

3.5.5   Emerging groundwater contaminants

There are many types of newly emerging contaminants found in groundwater that arise from human activities.

Examples are.

Pharmaceutical compounds which include all human and veterinary drugs.

Personal care products which include a wide range of compounds, including cleaning fluids, sunscreens, insect repellents, etc.

Pesticide metabolites, many of which are often detected in groundwater at higher concentrations than parent pesticide compounds.

Water treatment by-products such as trihalomethanes (THMs) (O'Driscoll *et al.* 2018).

Nanoparticles, which comprise naturally occurring and man-made particles, including materials used in computers, cosmetics, medical devices, etc.

3.6 Contaminant behaviour in groundwater

Understanding potential sources of contaminants and how they behave and move in groundwater is essential for an efficient design of a groundwater monitoring programme that aims to assess their presence in an aquifer and their impact on potential water use after abstraction. The types of potential groundwater contamination at specific locations is highly dependent on activities within the catchment, i.e., human settlements, industry and agriculture. Transport processes within groundwaters can disperse contaminants arising from these activities. Both dissolved and colloidal contaminants are highly mobile and can be transported downwards by rainwater infiltration and laterally by flowing groundwater. They may emerge in streams or in groundwater pumping wells.

Contaminant release can be a single event, such as an accidental spill, or intermittent, or continuous (Fig. 3.2). As a contaminant moves away from the source, several processes can occur which reduce

Figure 3.2 Movement and dispersion of a plume of soluble contaminant from a) a spill, b) an intermittent source, and c) a continuous source
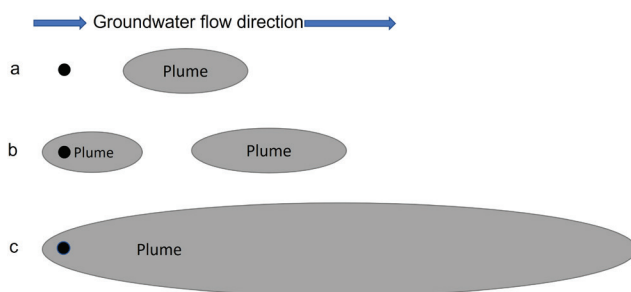
its concentration. The contaminated water may mix with clean water (which comes from other non-contaminated regions or from deeper in the aquifer), it may become sorbed to the aquifer solids, or it may decay. The impacts of these processes in contaminant attenuation at the point of water abstraction are highly dependent on the flow rate and the rates of retardation or decay of the contaminant.

The movement and location of a contaminant in the dissolved phase in relation to the source depends on the nature of the source and transport processes in the groundwater. The three main contaminant transport processes that redistribute dissolved materials over time are advection, dispersion and diffusion. Advection occurs when the contaminant is transported by the flow of water in which it is dissolved. The contaminant forms a plume which gets broader along, and perpendicular to, the flow path (Fig. 3.2). The direction and rate of transport coincide with that of the flow of the groundwater. Although advection is the dominant process controlling contaminant transport, diffusion and dispersion contribute to the spread of the plume. Dispersion causes the plume to spread out in all directions but does not slow the movement of the centre of mass. Mechanical dispersion arises due to the tortuosity of the pore channels in a granular aquifer and of the fissures in a fractured aquifer. It is also aided by different velocities of groundwater flow in channels or fissures of different widths. Molecular diffusion is the process in which the dissolved contaminants move from areas of higher to lower concentrations and occurs due to the concentration gradient; no flow is required. This is a very slow process and is only important at low velocities.

Through sorption certain contaminants can partition from the aqueous phase and bind to the surface of rock and sediments. Sorption is a surface equilibrium phenomenon; contaminants sorb when their concentration in water is higher, and desorb when their concentration in water is lower, than at equilibrium. The equilibrium state occurs when the distribution coefficient (K_d) is reached. Hydrophobic sorption occurs when poorly soluble organic contaminants adsorb to organic matter in sediments. Electrostatic sorption occurs when positive metal cations are attracted to clay minerals with net negative surface charges.

The movement of contaminants that are immiscible with water is governed by the density and viscosity of the fluid. Non-Aqueous Phase Liquids (NAPLs) form a separate phase in the pore network (e.g., petroleum liquor). They can be distinguished into two types: Light Non-Aqueous Phase Liquids (LNAPLs) are less dense than water and tend to float on the water
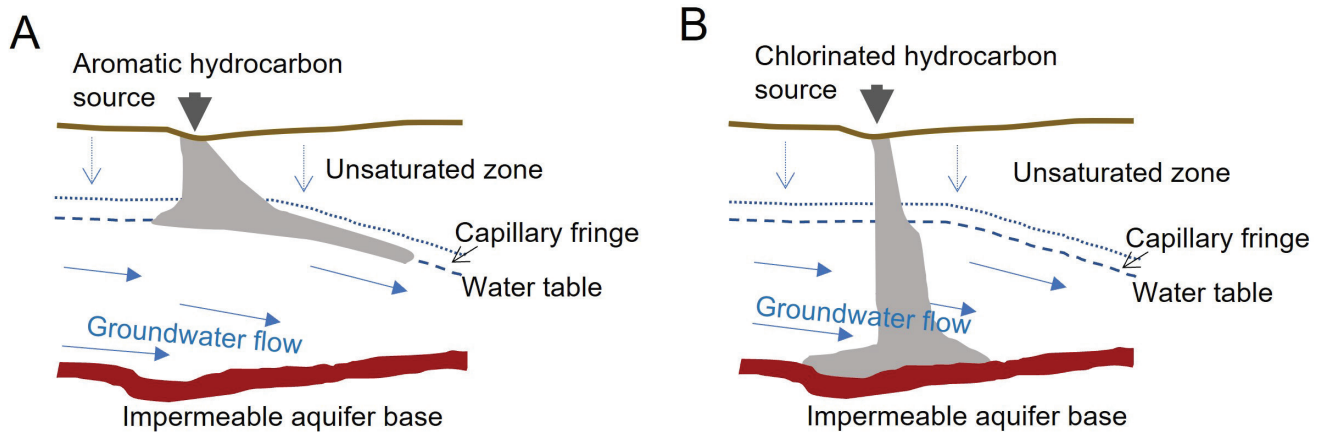
Figure 3.3   Movement of hydrocarbons following a surface spill

table whereas Dense Non-Aqueous Phase Liquids (DNAPLs) are more dense than water and tend to sink to the bottom of an aquifer. NAPLs usually do not migrate far in the subsurface, because they are too viscous and stick to mineral particles. However, all NAPLs are soluble to some extent and, when in contact with groundwater, a plume of dissolved substance is produced (Fig. 3.3). Moreover, some NAPLs are sufficiently volatile to produce vapours which can migrate to the surface and into buildings. Aromatic hydrocarbons tend to accumulate at the water table because they are less dense than water and more viscous (see Fig. 3.3A). They can rise as water levels rise but may remain in the unsaturated zone due to surface tension in pore spaces when water levels fall. The higher density and lower viscosity of chlorinated solvents results in them moving rapidly downwards into aquifers, where they may remain in depressions, regardless of the water flow (Fig. 3.3B).

3.7 Summary

- Groundwater quality depends on the geology of the aquifer and the presence of any contaminants.

- Chemical processes can occur within the aquifer and in the unsaturated zone that may change the nature of the water as it moves vertically and horizontally.

- Groundwater is threatened by many human activities that give rise to chemical and microbiological contaminants that can affect the potential use of the water, especially use for human consumption.

- Some contaminants arise from the natural geology of the aquifer, such as fluoride and arsenic.

- Different types of contaminants behave differently in the saturated zone depending on their chemical properties.

- Often the parameters that need to be determined at the lowest concentrations are also those which are least stable in aquifers and during the groundwater sampling process.

CHAPTER 4

GROUNDWATER MONITORING AND ASSESSMENT

4.1 Introduction

As outlined in chapter 1, there are several steps involved in planning and implementing a freshwater quality monitoring programme. The full chain of activities (Fig. 1.1) culminates in an assessment of the water body that provides information that is required for management of the resource. Monitoring comprises the activities that collect the data on quality and quantity, and assessment interprets those data in the context of known or potential influences on the resource. Therefore, in order to make a full assessment of groundwater quality, it is essential to have information on the hydrogeological context of the groundwater, together with sources and types of groundwater contaminants within the catchment. This information should be obtained in a preliminary assessment that assists in the design of the monitoring programme (see Chilton 1996), such as by suggesting the parameters to be monitored and the locations in which new boreholes may be required.

One of the most important aspects of any monitoring programme is deciding on the purpose of the monitoring and its associated objectives. All the field and laboratory activities must then be planned to ensure that these objectives are met. Examples of objectives for groundwater quality monitoring include:

- To determine whether abstracted groundwater meets quality criteria for specified uses. These criteria are usually defined by standards and regulations.

- To establish baseline water quality with which changes in quality and their trends can be compared.

- To understand the groundwater resource at national level so that it can be managed, and protected if necessary, for future sustainable use.

- To identify sources and extent of groundwater contamination.

- To assess the effectiveness of groundwater management activities.

Poorly defined objectives lead to poor quality information. It is important, therefore, that the monitoring objectives are clear before the monitoring programme design is finalised and monitoring commences. Over time, the objectives may change, and in this situation it is necessary to review the design of the monitoring programme and make adjustments to ensure the revised objectives can be met. Only after clear objectives are established, can the sampling programme be defined because all aspects of the design and planning are governed by the monitoring and assessment objectives. The sampling network will be influenced by the history of the aquifer (e.g., land use) and local aquifer conditions. Consideration must be given to monitoring well location and whether to use random, clustered or grid sampling, as well as the number of monitoring wells needed and whether to sample up- or down-gradient. The parameters that should be monitored, and the

frequency of sampling and analysis must also be decided, but together with the choice of sampling locations, they are extremely likely to be influenced by the availability of financial and human resources. The optimum monitoring network may not be achievable immediately but should be planned so that it can be implemented in a phased way as resources become available.

Factors that should be considered when planning a groundwater sampling network are summarised in Table 4.1 and elaborated in more detail in the following sections. As for all monitoring activities, human resources are essential, and it is expected that

both women and men will be involved in monitoring and assessment activities. For detailed coverage of approaches to groundwater monitoring and assessment, including examples and case studies, see Chilton (1996).

4.2 Selection of parameters and sampling methods

The parameters to be included in a groundwater monitoring programme depend entirely on the programme's main objectives. In order to characterise an aquifer system, for example, major ions are

Table 4.1   Factors to be considered when planning different aspects of a groundwater monitoring programme

Type of sampling location	Density of sampling locations	Sampling frequency	Parameters to be included
Complexity of hydrogeology	Complexity of hydrogeology	Residence time	Water uses
	Aquifer distribution	Seasonal influence on hydrology	Water quality issues
	Land use	Statistical considerations for assessment	Statutory requirements
	Statistical considerations for assessment		

Source: Based on Chilton (1996)

Table 4.2   Key parameters that may be included in a groundwater monitoring programme, depending on the objectives

Physical, chemical and microbiological	Major ions	Minor ions and trace elements	Trace organic compounds	Dissolved gases	Miscellaneous
pH electrical conductivity (EC) total dissolved solids (TDS) biochemical oxygen demand (BOD) chemical oxygen demand (COD) faecal coliform bacteria (e.g. *Escherichia coli*)	calcium (Ca) magnesium (Mg) sodium (Na) potassium (K) bicarbonate (HCO_3) sulphate (SO_4) chloride (Cl) nitrate (NO_3)	iron (Fe) manganese (Mn) fluoride (F) lead (Pb) arsenic (As) copper (Cu) zinc (Zn)	chlorinated solvents fuel hydrocarbons pesticides emerging micropollutants	oxygen carbon dioxide hydrogen sulphide	Isotopes chemical tracers

most relevant. For a pollution investigation, trace inorganic and organic compounds may be important, depending on the types of pollutant being investigated. As discussed in section 3.4, major ions can change along the groundwater flow system, particularly where interaction with carbonate aquifers increases mineralisation. It is useful, therefore, to include major ions in most groundwater monitoring programmes. Where abstracted groundwater is intended for human consumption, it is important to include microbiological indicators, especially if the aquifer is vulnerable to human and livestock waste. The inclusion of other potential contaminants that might present a risk to human health, such as nitrate, pesticides or arsenic, depend on the land use within the groundwater catchment and on the local geology. Ideally, the potential sources of contamination and the extent of their influence on the groundwater can be obtained during a preliminary survey as mentioned above and from any existing monitoring data. Table 4.2 suggests some key parameters that should be considered for inclusion in the monitoring programme.

The approach to sampling depends on access to the groundwater and the parameters to be measured. Some measurements can be made in the field (see section 4.5) and others may require careful sample handling and specific sampling techniques. There are three approaches: (i) taking a sample from a tap or pump connected to a groundwater supply well, (ii) taking a grab sample from depth using a special sampler such as a bailer, and (iii) bringing water to the surface using a pump. Sampling from an existing supply well is straightforward because the water can be collected directly into appropriate sample bottles. A supply well that is used frequently would give a more representative sample than a well that is used infrequently, because the water will be constantly refreshed and therefore more representative of the aquifer. However, contact of the sample with air during collection from a tap, for example, can lead to chemical changes and loss of unstable parameters; this should be taken into consideration when planning the sampling. A grab sampler is a device that can be lowered to the required depth and then closed, so that it captures a sample from the chosen depth before being raised to the surface. Some alteration of the chemical nature of the

sample is also likely when bringing it to the surface and transferring it to a container. There are numerous types of pumps that can be used to draw water from depth, depending on the depth to be sampled, the volume of water required, whether the pump needs to be easily portable, and the degree of sample integrity required. As for all water quality sampling, it is necessary to consider the material from which the sampling device is constructed and to ensure there is no risk of the sample being contaminated by the device with any chemical compounds that may interfere with the analysis for which the sample is being collected. Full coverage of this topic is beyond the scope of this guidebook, but further information can be found in Chilton (1996) and in many national guides available on-line, for example Weaver *et al*. (2007) and Sundaram *et al*. (2009).

A complete sampling protocol must include the desired parameters, together with the locations in which these parameters will be analysed, i.e., whether in the field or in the laboratory. The protocol should specify sampling techniques, sampling containers, sample pretreatments and sample transportation conditions. There are many factors which can influence the accuracy of the reported value for a certain parameter during or prior to laboratory analyses. These may be due to (i) inappropriate sample collection, storage and preservation, (ii) absence of pre-treatment where it is required (e.g. filtration, distillation), (iii) insufficient analyst training and/or lack of familiarity with the particular test procedure, (iv) issues with instrument calibration and reagent quality, (v) issues with instrument maintenance and laboratory conditions, (vi) bias in test procedure (e.g., interference from other compounds), and (vii) random (i.e., uncontrollable or uncharacterised) errors. Appropriate quality control procedures should be specified for all stages of the sampling and analysis process. Details of protocols for quality assurance of field and laboratory analyses are given in the companion guidebook on *Quality Assurance for Freshwater Quality Monitoring*.

4.3 Sampling locations and depth

Decisions on where to take samples for groundwater quality analysis are usually based on a combination

of factors, taking into account the objectives of the monitoring programme. These factors include:

- The hydrogeology of the area

- Access to boreholes, wells or springs in relevant locations

- Financial and human resources

- Known or anticipated sources of contamination

For a national evaluation of groundwater quality, it is important to have sampling locations that represent baseline quality and others that can show the potential influence of human activities, such as urbanisation and agriculture over time. It is also important to obtain a three-dimensional understanding of the groundwater quality and to identify links between groundwater and surface water. A routinely monitored national groundwater network should also be able to provide early warning of pollution in recharge areas. If contamination is suspected, or needs to be investigated in detail, it would be necessary to consider the source and distribution of the contaminant and whether it is related to a point or diffuse sources, and to select additional monitoring locations accordingly. Consulting local communities, including women who are tasked with water collection in areas not served by water distribution networks, could provide valuable background information. Sampling may need to be carried out beneath the land from which the contamination is arising, as well as at some sites above, i.e., upgradient of the source in order to obtain background (i.e., uncontaminated) water quality for comparison (Chilton 1996).

Existing wells supplying domestic, municipal, irrigation or industrial uses can be used for groundwater sampling, as well as springs and specially constructed monitoring wells (see section 4.6). The practicality, cost and technical aspects of each of these are summarised in Table 4.3 (UNEP 2020). When relying on existing monitoring locations it is important to check that there are no potential activities close to the well or borehole that may compromise the representativeness of the sample obtained. Examples include, poorly constructed and protected wells vulnerable to surface run-off (such as open dug wells)

and the likelihood of contamination from latrines or septic systems if the water table is high. One of the main disadvantages of using existing wells is that there may be little information available on the depths of the wells, the screens and the pumps. Information may also be lacking on water levels, construction materials, and pump discharge rates and times (UNEP 2020). This information is important because some wells may draw shallow, polluted groundwater from the upper part of an aquifer, others may draw it from less polluted deeper sections, or even from different aquifers in a layered sequence (UNEP 2020). If possible, when using existing wells for monitoring, those for which construction data are available, should be used.

Springs are cheap and easy to sample and can be representative of major groundwater bodies. Large springs have reliable discharges even in the dry season but small springs may be fed from shallow water sources and are therefore more vulnerable to local contamination. Springs may be the only monitoring option in some karstic limestone areas, where groundwater movement may be largely restricted to fractures and conduits connected to spring discharges (UNEP 2020).

Where no wells or boreholes exist in the required location, new monitoring boreholes may have to be constructed (section 4.6). Their use requires considerable capital and technical resources for construction and for sampling (Misstear *et al*., 2017). Such boreholes are widely used for monitoring local groundwater conditions around sources of groundwater pollution such as landfills.

Groundwater flow occurs in three dimensions (see section 2.4), and different pollutants under certain aquifer conditions may follow different flow pathways. Shallower pathways are more significant for flow and contaminant transport in less productive aquifers, because the bedrock is less permeable at depth. In more productive aquifers, with deep permeable zones, contaminants can move along deeper pathways. In addition, a reactive contaminant, such as phosphorus, that sorbs onto soil particles will generally follow a shallow pathway (e.g., overland flow, interflow), whereas a more soluble and relatively non-reactive pollutant, such as nitrate, will often leach downwards

Table 4.3   Characteristics of potential groundwater sampling points

Sampling Point	Advantages	Disadvantages
Municipal supply well	cheap and easy to sample repeat sampling, regular visits high discharge, representative of quality in the aquifer pumps usually operating may have existing time series data	possible uncertain construction and sample source, mixed water from several depths possible long time-lag after pollution has occurred locations fixed by population distribution, skews spatial coverage municipality/water company may not allow sampling
Irrigation well	as first three above, but less likely to have existing time series	as first two above, but less likely to have construction data spatial coverage skewed to agricultural areas may operate seasonally only
Industrial well	as for irrigation well above	as for municipal well, but less likely to have construction data
Domestic well	cheap and easy to sample repeat sampling, regular visits	low, intermittent discharge, especially with a handpump may need purging to remove stagnant water from within the well may be broken down and not pumping may be shallow and less representative of the aquifer vulnerable to very local pollution
Shallow monitoring borehole	may provide early warning of pollutants arriving at the water table repeat, regular sampling construction likely to be fully known inert materials can be used	moderate construction costs needs pump to collect sample care needed to remove stagnant water not very representative of the aquifer
Multi-level piezometers	construction should be fully known inert materials can be used early warning of pollutants at water table may indicate vertical stratification of groundwater quality may indicate vertical head differences and up or down movement of water	high construction costs needs specialist contractor and materials may be difficult to install correctly with good seals between sampling intervals requires special sampling devices and skilled operator
Springs	cheap and easy to sample repeat sampling and regular visits large springs may be representative of significant bodies of groundwater springs used for public supply may have existing time series data	vulnerable to local pollution sources may be vulnerable to direct rainfall small springs may represent superficial flow

Source UNEP (2020)

and follow deeper groundwater pathways. It is important to consider these aspects when designing a groundwater monitoring programme and to specify the depths from which samples should be taken accordingly. It may be necessary to use single or multi-level wells (see section 4.6). The length of well screens will depend on local aquifer conditions, i.e., aquifer types, aquifer depths, and presence or absence of impermeable layers between aquifers. Guidance on the use of multi-level wells and screen length for monitoring in relation to different objectives is available in Environment Agency (2006) and is summarised in Table 4.4.

Table 4.4   Use of multi-level wells and different screen depths in relation to groundwater monitoring objectives and aquifer conditions

Monitoring objective(s)	Aquifer conditions	Use of a multi-level well	Screen length		
			Very short (<1 m)	Short (1-2 m)	Long (>3 m)
Monitor general background aquifer quality	thick aquifer	Appropriate	Not appropriate	Appropriate	Most appropriate
Monitor general background aquifer quality	thin aquifer	Not appropriate	Appropriate, but not ideal	Most appropriate	Appropriate, but not ideal
Monitor light non-aqueous phase liquid	any	Not appropriate	Not appropriate	Appropriate	Most appropriate
Monitor dense non-aqueous phase liquid	any	Not appropriate	Appropriate, but not ideal	Most appropriate	Appropriate
Detailed examination of contaminant distribution	any	Most appropriate	Appropriate	Appropriate	Not appropriate

Source: Adapted from Environment Agency (2006)

Monitoring water in the unsaturated zone can provide early warning of contamination, especially for diffuse agricultural sources and from waste disposal facilities (Chilton 1996). Samples can be obtained by drawing water into a chamber with a vacuum, by using free-draining pan lysimeters, or by extraction by centrifugation of drilled cores.

4.4 Frequency of monitoring

The long residence times and slow rate of change in groundwaters means that less frequent sampling is necessary compared with surface waters. Confined aquifers and those with very old groundwater without active recharge can be sampled once a year. Sampling as part of a national programme to evaluate groundwater quality status and trends can also be done once a year for large groundwater bodies. Higher frequencies of two or four times a year may be needed for smaller aquifers and shallow groundwaters which are sensitive to seasonal influences from

rainfall, recharge, pumping for irrigation, and urban impacts. Samples should be taken before and after the rainy season and/or at the times of high and low groundwater levels. Karstic limestones should be sampled at least four times per year (UNEP 2020). Pollution source monitoring may require frequent sampling, depending on the local hydrogeological conditions, and especially if it is close to a potable water supply in a highly vulnerable aquifer with rapid fissure flow (Chilton 1996).

4.5 Field operations

Bringing groundwater from depth to the different pressure, temperature and oxygen conditions at the surface can alter its character. Therefore, it is preferable to carry out measurement of unstable parameters *in situ*, i.e., in the field. Field analyses are also important for giving a quick general indication of water quality. Typical parameters that are measured on-site are temperature, electrical conductivity

(EC), acidity and redox potential (Eh), together with measures such as alkalinity and dissolved gasses (e.g., O_2 and H_2S). These field measurements often require the well discharge to be passed through a throughflow cell to prevent the sample from being exposed to air during measurements. Portable laboratories (with titration kits, colorimetric kits and/or field incubators) are also widely used to carry out groundwater analyses in the field where the distance to the laboratory could compromise the samples and hence the results obtained. Moreover, it is important to note that for the accurate measurement of certain parameters, sample filtration and acidification is required *in situ* before transport to a laboratory for analysis.

It is important to remove stagnant water from the well before sampling to ensure the sample is taken from the aquifer rather than the well column. This is known as purging the well. Traditionally, a minimum of three well volumes need to be removed but more specific guidance is available in ASTM (2006). However, it is possible to check that sufficient water has been purged by monitoring the discharge temperature and conductivity until a stable reading is achieved that represents the aquifer water.

It is necessary to collect relevant hydrogeological data throughout the monitoring programme because this information assists with the interpretation of analytical results. This includes the routine measurement of groundwater levels in observation wells, often by taking spot measurements. Locally, changes in the water table or piezometric level can be very important, especially where there is a problem of salinisation associated with irrigation. Local changes in abstraction can also affect groundwater flow patterns, and climate data and infiltration rates can be relevant where leaching may occur from waste disposal sites or infiltration after fertiliser application.

4.6 Planning new monitoring wells

The design of any new monitoring wells must take into account the purpose of the wells, site location, geological succession (i.e., the series of strata and/or rock units at the location of interest), the nature of the aquifer under observation, the type and distribution of contaminants, and the depth of the borehole (i.e., drilled well). As groundwater tends to move from a recharge area on high ground towards a discharge point like a river, monitoring wells are often located along a transect at right angles to a riverbed.

When designing boreholes for groundwater monitoring, attention must be given to the location and length of the well screen. The screen is the filtering device that permits water to enter the well while preventing sediment ingress (Fig. 4.1). When the borehole is intended for monitoring, a long screen section should be avoided, because this may allow mixing between clean and polluted water from different depths in the aquifer. Screens should normally be less than 2 m in length.

If the objectives of the monitoring and assessment programme require knowledge of the vertical distribution of the water quality, multi-level sampling wells are needed or a cluster of boreholes reaching to different depths or in different aquifers.

4.6.1   Single- and multi-level well designs

In multi-layered aquifer systems, extra care must be taken during borehole installation to avoid cross-contamination between layers. Even a relatively short, single borehole design can lead to undesired inflows and outflows between the well and the aquifer system. Thus, a single-level design (i.e., a well that obtains data from just one aquifer layer as in Fig. 4.1) should be avoided if the aquifers exhibit strongly contrasting hydraulic heads or water quality characteristics. In these situations, a multi-level well is more suitable.

A multi-level, also known as multiple completion or multi-depth, well (Fig. 4.2) is a single borehole from which data can be obtained from different strata, at varying depths. These can be installed where a sedimentary aquifer system comprises several aquifer layers separated by aquitards or aquicludes. In this design a nest of piezometers is installed in one borehole, each with a single short length of screen targeted at a single aquifer, and separated from the other screens by an "impermeable" annular seal, often of bentonite clay. A multi-level well should prevent short-circuiting of waters of different hydraulic heads up or down the borehole (Misstear *et al*. 2017).

Figure 4.1   Simple schematic of a single-level monitoring well (adapted from Misstear *et al.* 2017)
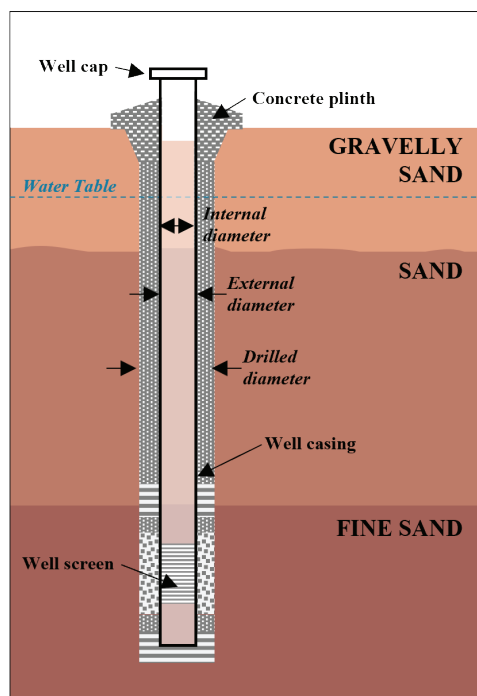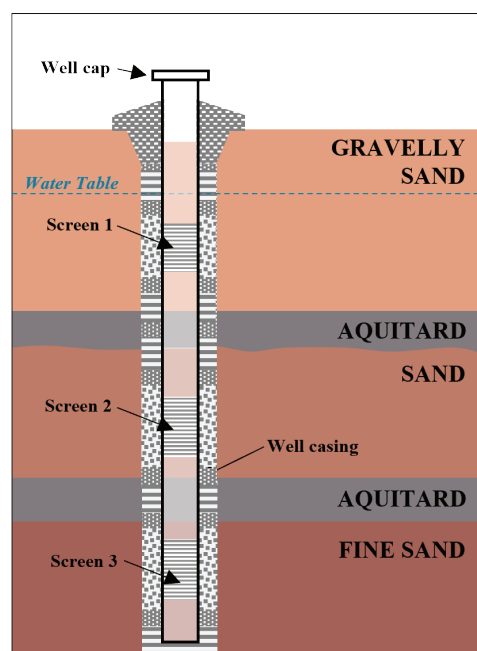

Figure 4.2   Simple schematic of a multi-level monitoring well (adapted from Misstear *et al.* 2017)

Any variation in groundwater quality through the thickness of the aquifer system can be monitored from these multi-level wells, in both consolidated and unconsolidated aquifers. Permanent observation well installations can be created by using specialised multi-port tubing and packer arrangements (Misstear *et al*. 2017). Multi-level well designs have the disadvantages of being more complex and expensive than single-level wells, and the seals may not be effective. The more reliable alternative is to drill a borehole cluster, with screens located in different aquifers; however, this option is even more costly.

4.6.2   Construction of borehole

A key borehole characteristic which must be established prior to drilling a monitoring well is its internal diameter (ID). This must be large enough to accommodate any proposed sampling and monitoring equipment. An ID of 50 mm, for example, is suitable for some depth samplers such as the specialised slim sampling devices available on the market, and low-capacity pumps. An ID of 100 mm permits a greater range of sampling equipment and geophysical logging tools. However, IDs greater than 100 mm may make it difficult to purge the borehole adequately (i.e., remove the stagnant water from the borehole casing prior to sampling) with a low-capacity pump. Once the ID is established, the drilled diameter for the borehole can be calculated. Its value must be 50-100 mm greater than the maximum outside diameter (OD) of the well casing (see Fig. 4.1).

It is very important to choose construction materials that do not react with the contaminants being monitored in samples taken from the well, in order to avoid "false negatives" or "false positives". Therefore, the casing and screen materials should neither adsorb pollutants from the groundwater, nor leach substances into it. Steel casings, for example, can react with metallic elements in the well water, while certain plastics can react with organic compounds. The material most commonly used in contaminant investigations is polyvinyl chloride (PVC), because it is considered suitable for many applications. However, it should not be used where, for example, organic compounds are present as non-aqueous phase liquids (Fetter *et al*. 2018). Some of the

Table 4.5   Advantages and disadvantages of different well design materials

Material	Advantages	Disadvantages
Mid or low-carbon steel	Strong, rigid, inexpensive	Liable to corrode and leach metallic constituents May sorb metals (especially on corrosion sites
Stainless steel	Strong, corrosion-resistant, good chemical inertness (organic)	Expensive May leach chromium or other metal elements
PVC	Rigid, light, inexpensive, good chemical inertness (inorganic)	Not as strong as steel May react with organic compounds in water Not suitable where non-aqueous phase liquids are present Temperature-sensitive compared to steel
Polyolefins, including polypropylene and high-density polyethylene (HDPE)	Light, inexpensive, good chemical inertness (inorganic)	Not as rigid as PVC May react with organic compounds in water Temperature-sensitive compared with steel
Fluoropolymers	Light, very good chemical inertness	More expensive Not as rigid as PVC More difficult to handle than other plastics Low tensile strength of joints May sorb certain organic compounds

Source: Adapted from Misstear et al. (2017)

advantages and disadvantages of commonly used materials are summarised in Table 4.5.

4.6.2 Avoiding cross-contamination during well drilling

Cross-contamination is a serious concern when drilling monitoring wells. Precautions to avoid this must be taken, particularly between different borehole sites, and between different layers within the same borehole. Measures may include steam cleaning a drill rig between borehole sites, and flame cleaning drill tools prior to each placement down a borehole. Moreover, it is essential with all well drilling activities that these are properly supervised by a hydrogeologist or engineer. Otherwise, serious issues may arise, such as the monitoring well being poorly constructed or the screen being set to the wrong level, both of which can lead to cross-contamination. The supervisor's role is to ensure that the drilling method and procedures are

appropriate for the proposed well design, that good formation samples are collected and logged, that the final well is properly developed (i.e., cleaned out), and that the entire system is tested before commissioning.

4.7 Summary

- Well defined objectives are essential for an efficient and meaningful groundwater monitoring programme.

- Gathering preliminary information about land use distribution and human activities can contribute to the selection of appropriate locations for sampling and the optimum list of parameters to be measured.

- It is important to obtain baseline chemical characteristics for the aquifer with which future changes in water quality can be compared.

- A three-dimensional conceptual hydrogeological model to show rock types and how groundwater occurs and moves, should underpin the development of a groundwater quality programme.

- If necessary, hydrogeological expertise should be sought to assist with creating the hydrogeological model for both local monitoring of known pollution sources or regional or national monitoring.

- Sampling may need to be carried out at different depths in the aquifer as well as in recharge and discharge zones. Specific sites may need to be selected up gradient and down gradient in relation to the sources of known contamination.

- Existing wells used for water abstraction, springs or purposely drilled monitoring boreholes can be used to collect samples, although each has advantages and disadvantages.

- Samples can be collected using existing taps or by using grab sampling devices or pumps, depending on the depth from which the sample is taken.

- Some parameters should be measured *in situ* to avoid potential changes that occur when samples are brought to the surface and transferred to sample containers.

- Sampling is usually only necessary once or twice per year, unless specific objectives require more frequent or continuous monitoring.

- Care must be taken when choosing the design of new wells and boreholes to ensure that they will be fit for purpose, whether for water supply or specifically for monitoring. Where the wells will be used by local communities, consideration must be given to ensure safe access, especially for women and girls in rural areas.

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