CHAPTER

# 1

# Hydrodynamics and geomorphology of groundwater environments

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## Introduction

Within the global water cycle, the groundwater pool represents a substantial volume of water, containing approximately 8,000-23,000•$10^3$ $km^3$ (Abbott et al., 2019). Annual groundwater discharge to the ocean (0.1–6.5•$10^3$ $km^3$/year) is two to three orders of magnitude smaller than oceanic evaporation (350–510•$10^3$ $km^3$/year), which initiates the continental part of the water cycle through atmospheric condensation and landward precipitation (88–120•$10^3$ $km^3$/year). The other segments of the water cycle are part of our daily life: the clouds in the sky, the polar ice seen from satellites and the snow, closer to us, the rivers we like to walk along, and the lakes where we go fishing and swimming. Conversely, the underground part of the water cycle remains poorly known to the general public. It is the invisible part of the water cycle. In fact, for many people, the notion of groundwater is generally associated with the idea of an underground lake or river. Instead, groundwater is a sponge-like hydrologic system that occupies an extensive network of voids in near-surface (crustal) rocks of the continents and ocean floor. While groundwater systems are understood conceptually, less is often known about the specific movement of water through the subsurface system and the associated annual water cycle.

Groundwater has long been difficult to comprehend in its entirety due to its subterranean nature and difficulty of access. Geologic maps offer clues for determining where groundwater may occur as a function of different rock types, sedimentary deposits, and surface topography,

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but the spatiotemporal extent of groundwater can only be measured from boreholes/wells and cave/spring systems, which are typically limited to a relatively small number of locations.

The underground hydrologic system is dynamic, made up of numerous flow paths (Fig. 1.1). The nature of these flows is complex, in response to the strong heterogeneity (spatial variability) of geological formations and, in turn, their ability to hold and transfer water (*permeability*). The soil (top layer of the sediment) constitutes the first compartment that controls flows feeding the groundwater system as a result of precipitation and snowmelt that percolate into the soil. Within a given groundwater system, we can find very fast flows, as well as areas with extremely slow flows. These variations can exist both on a regional scale and on a microscopic scale, with variations in flow controlling the physical and chemical interactions between water and rock. The physical control of water fluxes and the chemical control of elements are therefore intrinsically coupled.

Observed linkages between surface water and groundwater provide further information about the extent and function of the groundwater system, with recent studies emphasizing the need to evaluate river systems within the context of groundwater processes. For example, springs, which are a direct emergence of groundwater onto the landscape, can have important controls on headwater portions of the surface water system and downstream water quality (Peterson et al., 2001; Alexander et al., 2007; Meyer et al., 2007; Soulsby et al., 2007; Rhoades et al., 2021). Throughout their course, rivers also receive diffuse flows from the underground environment that modulate physical conditions. In turn, rivers drive complex exchanges of water between the surface and subsurface hydrologic systems. Consequently, surface water and groundwater are extremely dynamic, integrated systems.

Groundwater resources have become a subject of concern in the Anthropocene (the current geologic epoch in which humans have substantially altered physical and ecological processes (Crutzen, 2002), especially regarding climate change and pollution. Climate-driven increases in temperature and evapotranspiration may limit future groundwater volumes and the extent of groundwater flow. Weakening groundwater flows can have severe impacts on surface systems and may increase the length and occurrence of droughts. Drought, which occurs in nearly all regions, has affected more people worldwide in the last 40 years than any other natural hazard. The effects of water scarcity can manifest through environmental crises, as droughts may induce tipping points (Otto et al., 2020). As such, active research currently focuses on the effects of climate change on groundwater systems (Amanambu et al., 2020) given that a large number of human populations may have difficulty accessing drinking water under future climate scenarios. Human activities also can have major effects on the water quality of groundwater systems. Intensive agriculture can cause diffuse pollution of nitrate, creating extensive eutrophication (Vitousek et al., 1997; Tilman et al., 2001). Other pollutants entering groundwater systems, such as endocrine disruptors, nanoparticles, and microplastics, have become a major concern due to their impact on both human life and biodiversity (Kremen et al., 2002; Gallo et al., 2018).

Groundwater ecosystems also host a large variety of organisms that dwell in open spaces within the underground material, ranging from small pores or cracks to large voids and tunnels that are typically present in karst landscapes (e.g., limestone caverns) and lava tubes. The flows that traverse the underground environment also control the supply of nutrients accessible to living organisms. Porosity and flow, therefore, condition the subsurface living world and constitute an extremely diverse set of habitats in which physical, chemical, and biological systems are intimately interconnected.

The aim of this chapter is to describe the physical and chemical principles that characterize these underground environments. Specifically, we review the physical basis of aquifers (groundwater reservoirs), their hydrodynamics, and hydrogeological parameters (porosity and permeability) that collectively define different types of aquifers. We explore the relationships between groundwater and surface water and define how aquifers function in terms of (1) groundwater flow and the transport of solutes and particulate matter; (2) groundwater age, which affects ecosystem processes, physical and biological relations, and groundwater resources; and (3) modeling of the above processes. We also consider the chemical composition of groundwater and the origin of compounds and water—rock interactions that influence water quality. Finally, we discuss chemical and nutrient fluxes in aquifers and biogeochemical reactions, with a focus on oxygen and nitrogen.

## The aquifer concept

Most rocks, soils, and sediments near the surface of the earth have a certain degree of porosity caused by voids and fractures and, thus, are referred to as *porous media*. The ability of porous media to transmit water (*permeability*) depends on having connected pores. Permeable subsurface lithologies that contain extensive bodies of groundwater are termed *aquifers*. The upper surface of the aquifer is known as the *water table*, which separates saturated and unsaturated zones within geologic strata. In unconfined aquifers, the capillary rise may form a band of saturated sediment above the water table. This region is also known as a zone of tension saturation because tension forces pull the water upward into available pores, resulting in water pressures below atmospheric values in this zone. The capillary rise can extend above the water table from a few centimeters in sediments with large pores (e.g., clean gravel), up to several meters (e.g., 4—5m) in clay soils with small pores. Because the position of the water table varies with time due to seasonal and decadal changes in the supply and movement of groundwater, a variably saturated zone also can be defined (Fig. 1.1).

### Drivers of groundwater flow

The water content of the aquifer differs from the water flow, which is related to spatial gradients in the energy head. Water moves from high to low energy-head locations modulated by a conductivity coefficient describing the ease with which a given porous media transmits fluids. This phenomenon is described by Darcy's (1856) law

$$q = -K\frac{dh_T}{dl} \tag{1.1}$$

where $q$ is the flow per unit area (with dimensions of length, L, divided by time, T; L/T), $K$ is the hydraulic conductivity (L/T), $h_T$ is the total energy head defined as the sum of the hydraulic pressure head $h_p$, the elevation head $h_z$ (gravitational potential energy arising from elevation), and the velocity head $h_v$ (kinetic energy of the fluid velocity), all of which are expressed as the height of water (L), and $l$ is the distance (L) over which the change in $h_T$ is evaluated. Because interstitial flows through porous media tend to be slow, $h_v$ is typically

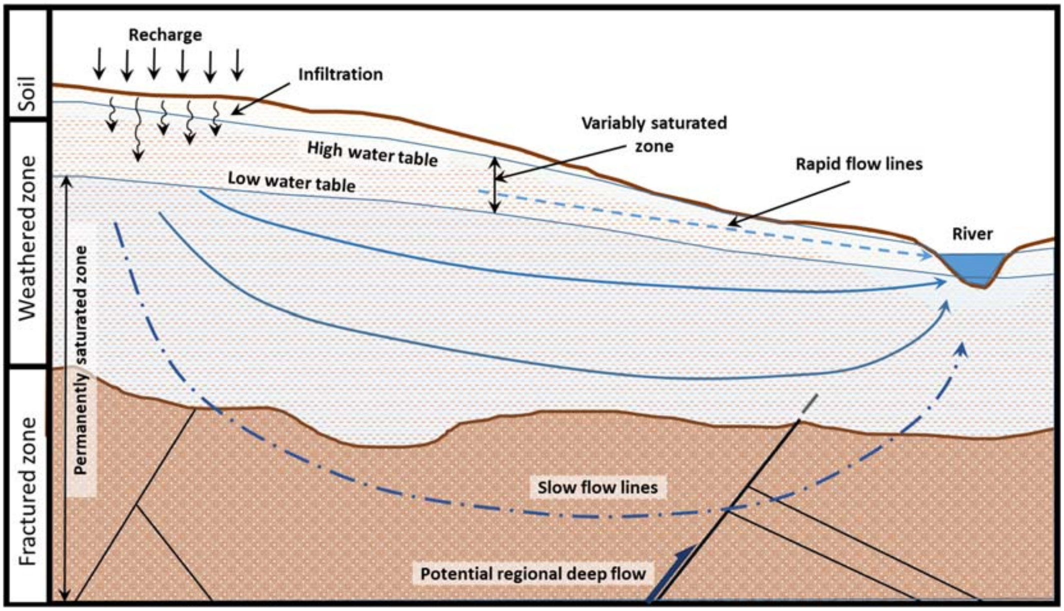


FIGURE 1.1 Cross-section of an aquifer. Blue lines with arrows show groundwater flow paths. Black diagonal lines portray main fractures.

negligible, such that $h_T$ is defined by the piezometric head $h_p + h_z$, which is simply the elevation of the water table measured by subtracting the depth to groundwater from the land surface. Consequently, it is the higher altitude of the water table within a landscape that creates groundwater motion, just like in a closed U-shaped tube with a difference in water level that is suddenly opened. Groundwater motion may be conceptually defined as successive flow lines that act as separate tubes (Fig. 1.1).

Figure 1.1 presents a cross-sectional view of a simple aquifer fully open to the atmosphere (*unconfined aquifer*), in which groundwater moves according to Darcy's law from the mountain top toward the river valley along three nested flow paths in the variably saturated, permanently saturated, and fractured zones, respectively. The variably saturated zone represents the seasonal variation of the water table due to competition between *recharge* and depletion of the aquifer. Recharge is mainly driven by precipitation percolating into the soil, but is modulated by vegetation. When precipitation infiltrates the soil, some water that is held against gravity in pores due to matric forces (i.e., adhesion of water to solid surfaces and the attraction of water molecules to one another) is accessible by plants and can be removed via evapotranspiration from this near-surface water reservoir. Particularly in summer and spring, plant demand progressively depletes the soil water content. Once the soil water content increases and gravitational forces exceed matric forces, water flows through the soil and the unsaturated zone down to the water table and into the aquifer. Over geologic time, the water within the aquifer weathers the bedrock to a certain depth, below which groundwater moves more slowly through fissures and fractures in the more competent (less weathered) parent bedrock (fractured zone). The rate of water movement (and thus its age) differs between the variably saturated, permanently saturated, and fractured (unweathered) zones due to differences in energy head, hydraulic conductivity, and the length of a given flow path (Fig. 1.1).

Aquifers may also be encountered below geological formations at depths of several hundred meters, particularly in sedimentary basins. Such geological formations also have limited zones of water inflow (recharge zones) and present extremely slow renewal rates. Although present at great depths, these aquifers represent active microbial ecosystems (e.g., Chapelle, 2001). The outflow of these systems also supports oases and specific groundwater-dependent ecosystems. Closer to the surface, aquifers may not be entirely open to the atmosphere, covered by clay-rich (low permeability) layers or geologic formations that cap and confine the aquifer. *Confined aquifers* can exhibit substantially different geochemical compositions and limited fluxes of nutrients, thus representing a different ecosystem within the aquifer compared to unconfined strata.

When aquifers are located at a great depth or close to a magmatic chamber in volcanic areas, temperature also becomes a driver of water motion and leads to the uprising and outflow of deep hot water (for example, geysers and geothermal vents). Indeed, volcanic areas are also the location of numerous thermal springs, which represent the outflow of hydrothermal convection cells. Thermal springs are frequent along mountain ranges, which induce large and deep hydrogeological loops of groundwater motion. In the deeper part of the loops, water encounters high temperatures and the upward movement of water is related to combined effects of thermal and head gradients. Such regional loops can also be present in nonmountainous areas, potentially with slight temperature anomalies (Fig. 1.2). This kind of hydrogeological situation is interesting as it induces mixing between deep and shallow groundwater with extremely different chemical compositions and biodiversity.

## Aquifer hydrodynamics

### *Porosity*

The total volume $V_t$ ($L^3$) of an aquifer can be divided into the volume of solids $V_s$ and the volume of voids $V_v$. The ratio of $V_v$ to $V_t$ defines the porosity $n$ (dimensionless) of the material, which is typically expressed as a percentage. There are several methods for determining porosity (Hao et al., 2008; Flint and Flint, 2018). Most commonly, it is determined by measuring the bulk density of the material and particle density of the solids. Other methods include obtaining a water-saturated sample of known volume and drying it in a laboratory oven (105°C). The difference in weight before and after drying (correcting for the temperature dependence of water density) gives information about the volume of water per total volume of the sample. For samples containing water that cannot be removed in a drying oven at those temperatures, the porosity can also be determined by sealing a sample of known volume with paraffin, placing it into the water, and measuring the displaced volume of water. The porosity gives the entire volume of the pore space, and thus gives information about the water volume potentially stored in an aquifer. However, a certain amount of pore space may contain entrapped air, rather than water, nor will all pores contribute to water flow due to, for example, dead-end pores, nonconnected pores, adhesively bound water, or hydrated water

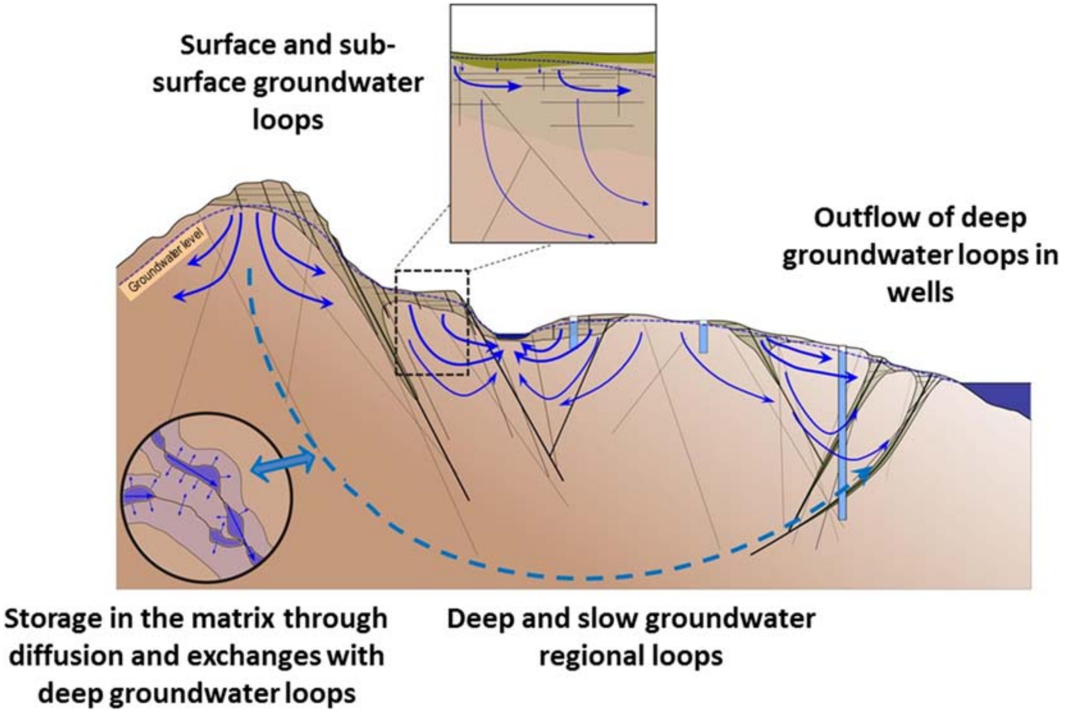


FIGURE 1.2 Different levels of mixing in aquifers. *Redrawn with permission from Fig. 1.14 of Roques (2013).*

of clay minerals. When considering only the amount of void volume contributing to the water flow, the volume ratio is denoted as an effective porosity $n_{eff}$. In addition, there is a distinction between primary porosity (i.e., that of the deposited sediment or parent rock material) and secondary porosity (i.e., that due to subsequent chemical or physical weathering). The latter is of particular importance in the weathered and fractured zones of bedrock aquifers, as well as in karst aquifers.

The value of porosity for unconsolidated material generally ranges from 25% to 70% (Freeze and Cherry, 1979) and is largely dependent on the size and shape of individual particles, and how well-sorted or uniform they are. Clay has higher porosity compared to sand or gravel, but is less permeable. For consolidated material, porosity values range from 0% to 50% (Freeze and Cherry, 1979) and are lower for crystalline rock or shale compared to fractured or karstic aquifers. When considering aquifers as habitat for organisms, the overall porosity is less important than the size of individual pores and the connectivity of the pore network. The pore size distribution defines whether aquifers are suitable habitats for biota, because they are restricted from actively moving or being transported through pores smaller than their own size (Fig. 1.3). Groundwater fauna is therefore mainly found in alluvial sediments with larger pores or in fractures or channels of fractured rocks or karst aquifers (Humphreys, 2009). However, it was found that some of these organisms not only use open voids, but are capable of modifying their environment by moving grains and digging through

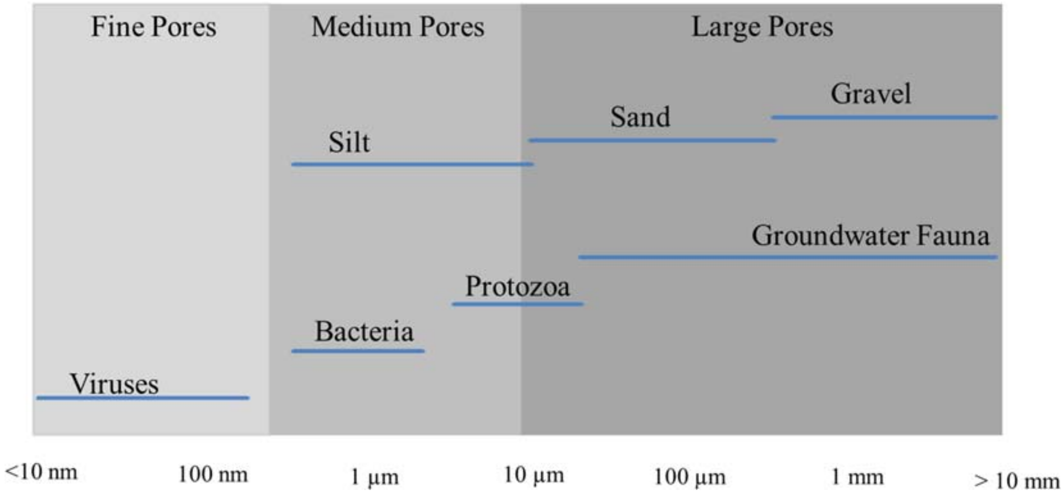


FIGURE 1.3 Pore size classes (fine, medium, and large) as a function of different types of unconsolidated material (clay, silt, sand, and gravel) in comparison with size ranges for viruses, bacteria, protozoa, and fauna in aquifers. *Modified with permission from Krauss and Griebler (2011) and Matthess and Pekdeger (1981), with fauna data from Stein et al. (2012) and Thulin and Hahn (2008).*

porous sediment (Stumpp and Hose, 2017; Hose and Stumpp, 2019) or by moving into clay sediment (Korbel et al., 2019). For bacteria and viruses, most pores in unconsolidated material are wide enough for them to either be dispersed in water or attached to solid surfaces (Fig. 1.3).

### *Permeability and hydraulic conductivity*

The pore size distribution not only forms a habitat for biota, but also dictates how fast water flows through an aquifer for a given head gradient, as described by Darcy's law (1). The velocity of groundwater moving through pores and fractures, in turn, influences the energy needed for an organism to forage and live in such environments. The smaller the pore, the larger the flow resistance and the slower the flux. For uniform material and a unit head gradient, the fluid movement is proportional to the square of the mean pore diameter (Fetter, 2001). The proportional factor between the head gradient and the water flux is defined by the hydraulic conductivity $K$ in Eq. (1.1). It combines properties of the fluid (viscosity and density) and of the sediment/rock material. The inherent property of the porous medium alone is its permeability $k$ ($L^2$), which is mainly controlled by the size distribution of the voids. Therefore, unconsolidated fine materials like clay, glacial tills, or silt have smaller permeability values ($10^{-19}$–$10^{-13}$ $m^2$) compared to coarser materials like sand and gravel ($10^{-13}$–$10^{-7}$ $m^2$) (Freeze and Cherry, 1979; Gleeson et al., 2011). For consolidated rocks, permeability is generally low ($10^{-20}$–$10^{-12}$ $m^2$) due to low porosity, particularly in the absence of secondary porosity features (fractures, channels). If such features are present and augmented by weathering of the parent rock, permeability is larger ($10^{-15}$–$10^{-9}$ $m^2$) and depends on how well those features are connected (Worthington et al., 2016).

Permeability and connectivity of pores also may affect the bioenergetics of organisms in terms of nutrient availability and foraging distances.

Typically, the permeability and the hydraulic conductivity of a given medium are spatially variable (heterogeneous) depending on the structure, competence, and composition of the sediments/rocks. This is referred to as *continuous heterogeneity* because it describes the spatial variability of hydraulic properties within a given facies (e.g., a mixture of sand and gravel) due to the connectivity of porosity and fissures, which differs from *categorical heterogeneity* that describes changes in hydraulic conductivity among different facies (e.g., sand vs. gravel bodies). Permeability and hydraulic conductivity are often vector properties, leading to different behavior in the horizontal versus vertical directions (*anisotropy*). Both heterogeneity and anisotropy make it difficult to accurately measure the hydraulic conductivity in a representative elementary volume (REV, a volume of sediment large enough to capture the intrinsic process variability, but small enough to avoid combining variability among sediment types). Pumping tests or any other methods for determining hydraulic conductivity quantify the effective hydraulic conductivity, a lumped property controlled by the sediment/rock features having the largest hydraulic conductivity. Nevertheless, such values provide bulk information about the environment of the well during the pumping test. For scaling hydraulic conductivity and connectivity of specific hydrogeological features, regionalization methods can be used (Renard and Allard, 2013).

## Geologic types of aquifers

The above discussion of groundwater flow lines within aquifers is idealized, describing conditions that might exist in relatively homogeneous material, where hydraulic conductivity does not change spatially. In reality, any porous media has morphological and chemical variations that cause spatial changes in hydraulic conductivity, such that aquifers are intrinsically heterogeneous, but the degree of heterogeneity may vary from low to high. Furthermore, the geologic and geomorphic history of the landscape can have a strong influence on aquifer properties and function, with heterogeneous aquifers common in both karstic and fractured bedrock terrains.

Karstic aquifers are mainly carbonate rocks (e.g., limestone), which are progressively dissolved by carbon dioxide ($CO_2$) contained in water that originates from the soil due to organic matter degradation (White, 2002). Karst landscapes constitute 12%–15% of the continental surface. They are characterized by various dissolution features within the strata, including shafts and sinkholes, some of which may be primary locations for the inflow of surface water to the aquifer drainage system. Sinking streams are also a major feature of karst geomorphology and have attracted substantial attention due to the dramatic and *flashy* nature of flow in this part of the system (i.e., rapid flooding and drainage). The unsaturated zone of karstic systems also differs from more homogenous aquifers, typically characterized by dissolution features that may create specific local porosity in the first few meters of the karst surface. This zone of intense dissolution is termed the *epikarst* and may constitute a near-surface reservoir for the karst system, where water stored in the epikarst slowly infiltrates and recharges the underlying aquifer (Aquilina et al., 2006; Williams, 2008).

Karstic aquifers are characterized by a drainage system that traverses the entire carbonate formation from surface input to outflow, which may be characterized by a complex series of springs or a single dominant channel that controls a large part of the system. The drainage system is spectacular as it constitutes cavities that can be explored not only from a hydrogeological point of view but also for recreation and tourism. Karst aquifers are also important groundwater ecosystems because they can support larger groundwater fauna, such as fish (e.g., Hancock et al., 2005). Within the main channels of the karst drainage system (typically large caves), water flow is extremely rapid and produces spectacular floods that are often described as major characteristics of karstic systems. These open water flows are highly sensitive to human activities. Although the main channels of karst systems are typically flashy, matrix water within the carbonate aquifer contributes to the flow during the entire hydrological year, supplying water to outflow springs even when there is no surface-driven flooding in the main channels. Within the karst matrix, the transit time of water (i.e., the length of time spent traversing a given flow path) is often much longer than that of the primary drainage system of caverns and carbonate tunnels, providing strong mixing between rapid and slow flows (Long and Putnam, 2004; Bailly-Comte et al., 2011; Palcsu et al., 2021). Higher hydraulic head during flood events can cause a substantial flux of matrix water (Screaton et al., 2004), making many karstic systems flashy by nature, although the water that is flushed out during floods may have residence-times greater than assumed from the rapid pressure response (Kattan, 1997; Katz et al., 2001; Stuart et al., 2010; Han et al., 2015).

Fractured bedrock aquifers are also highly heterogeneous systems (Neuman, 2005). Hard-rock geologies represent about one-third of the continental surface and their aquifers thus comprise major water resources in many countries. In these systems, water circulates within the discontinuities of the rock (e.g., faults, fractures, and fissures). In contrast, the bedrock matrix itself has extremely low porosity and permeability and does not constitute a major water reservoir. Groundwater flow paths in fractured systems follow energy head gradients as presented in Fig. 1.1, but with more complex flow lines due to the heterogeneity of the medium. The formation of aquifers in hard-rock geologies requires intensive weathering of the bedrock over geologic time. Thus, fractured aquifers are often described as a weathered layer a few tens of meters thick, overlying the more competent parent bedrock. The weathered layer typically has a high clay content and is characterized as a hydrologically capacitive stratum, susceptible to human activities (Dewandel et al., 2006; Ayraud et al., 2008). The fractured part of the aquifer represents the transmissive part of the system and is more protected from human activities due to its deeper depth. The interface between the weathered and fractured zones is referred to as the *weathering front* and is a particularly reactive layer that is more intensively fractured than the underlying bedrock. Both layers represent fundamentally different systems, with differing hydrogeological properties and chemical compositions. Indeed, they also represent quite different ecosystems, with different microbial communities (Maamar et al., 2015).

Karstic and fractured systems present a high degree of heterogeneity between their low-permeability matrix material (competent bedrock) and the highly permeable karst conduits or hard-rock fractures. However, heterogeneity is manifested by different features over scales that vary by several orders of magnitude (Fig. 1.4A–C). For example, large regional faults may be present over several tens of kilometers along the surface of the landscape that transition to more localized fault networks at depth, with lengths of tens of meters. At smaller scales, fissures and cracks constitute discontinuities around faults or mineral boundaries. At even smaller scales, microscopic cracks and discontinuities in minerals create porosity

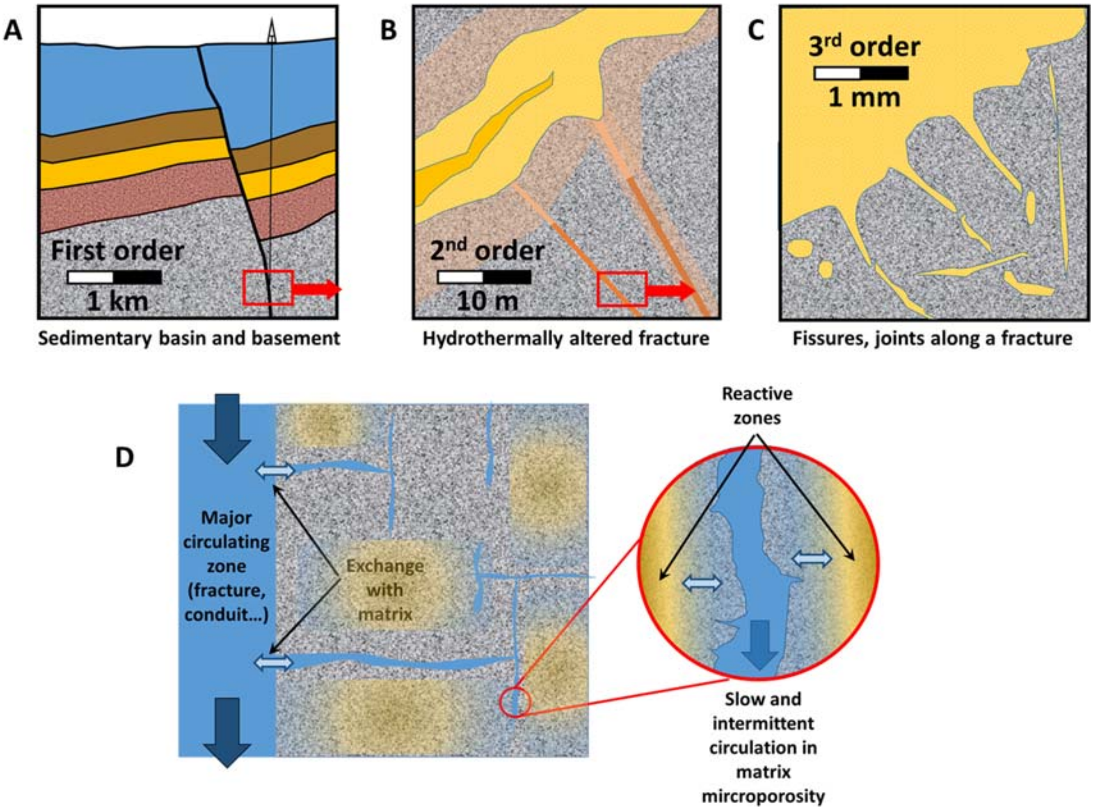


FIGURE 1.4 Heterogeneity in aquifers. Panels (A–C) show successive scales of heterogeneity in a fractured aquifer, while panel (D) shows heterogeneity and hydrobiogeochemical functioning in peat.

within the rock. All scales of discontinuities contribute to the whole–water content of the aquifer, but with different properties. Large faults or fault zones may allow substantial fluid flow that is relatively more rapid, while the microporosity may act as a fluid reservoir. This affects both the hydrologic and chemical properties of the system. Even within relatively homogeneous aquifers, heterogeneity is also the rule, rather than the exception. Sandy aquifers contain both clay-rich and coarse facies that present local heterogeneity that respectively slows or accelerates water fluxes due to differences in grain size and hydraulic conductivity. These structures may also present distinct mineralogy and chemical reactivity. Heterogeneity is highly important for biogeochemical reactions and thus microbial ecosystems. Beyond the mean chemical characteristics of a given aquifer (e.g., chemical composition, pH, and redox), microsites within the aquifer may have very different conditions. For example, peatlands may be flushed by fresh water, resulting in overall oxic conditions, but intense sulfate reduction may occur in the microporosity of the peat, away from the main water flow (Fig. 1.4D). This allows resilience of peat and wetland systems that support relatively frequent water renewal while ensuring reducing functions such as denitrification (Racchetti et al., 2011).

## Links to surface hydrology

Aquifers are intimately linked to the surface hydrological system within watersheds. Rainfall and snowmelt percolate vertically through hillslope soils, helping to recharge the aquifer. However, most of this surface input moves laterally downslope and mainly supplies water to lakes and rivers in alluvial valleys (Fig. 1.1). The sediment in alluvial valleys is typically porous, allowing continued connection with the aquifer as the surface water flows down valley toward an ocean or terminal lake (endorheic or sink basin). Where the water table of the aquifer coincides with the water surface of rivers, subsurface flow is directed toward the river, since it represents the local topographic low point (Fig. 1.1). However, if the river flow is perched above the aquifer's water table, the river water will be driven into the streambed, recharging the aquifer through percolation and vertical head gradients; in extreme cases, rivers may become seasonally dry, disappearing into their streambeds (ephemeral streams). These two conditions, in which the river either receives groundwater or contributes river flow to the aquifer, are referred to as *gaining* versus *losing* conditions, respectively. Such phenomena may vary seasonally as the water table of the aquifer rises or falls (Fig. 1.1), and the process applies to any surface water body (i.e., rivers, lakes, and wetlands). These conditions can also vary with climate, such that water bodies in humid regions are typically gaining, while those in arid regions are frequently losing. Water bodies in karst terrain are typically losing systems, with surface water descending into the aquifer through a variety of surface fractures/inlets (e.g., sinkholes/swallets, ponors, and shafts) (e.g., Monroe, 1970; Taylor and Greene, 2008).

Because of the porous nature of alluvial sediments, the entire alluvial valley can be connected to the aquifer. For example, when rivers spill onto the valley floor during floods, water may pond for extensive periods of time, with some of this water percolating into the alluvial sediment and recharging the aquifer. Conversely, head gradients may cause the aquifer to direct water onto the floodplain via springs and seeps, which typically occur at the break in slope between hillslopes and the river valley or at topographic lows in the floodplain. Processes and rates of exchange between surface water and groundwater also may be influenced by geologic and geomorphic history in terms of how rugged the landscape is (topographic gradients) and the nature and stratigraphy of the bedrock geology and alluvial deposits. For example, volcanic eruptions can fill valleys with lava or ash, both of which have very different porosity and hydraulic conductivities. Similarly, glaciers create broad U-shaped valleys filled with sediments ranging from boulders to fine clay, resulting in different boundary conditions than valleys formed by faulting in the absence of glaciation. Extensive glacial advance can also erase topography and reorganize the direction and magnitude of surface runoff that occurs in river networks. Finally, human activity in river corridors (e.g., dams, diversions, levees, groundwater pumping, agriculture) can alter both surface and subsurface hydrological cycles and, in the long term, may significantly deplete aquifer resources and alter surface and subsurface ecosystems.

Another important linkage between surface and subsurface water occurs through *hyporheic exchange*, which is the movement of river water into and out of the alluvium within the river valley over relatively short time frames and short flow paths compared to deep groundwater movement in the aquifer (Fig. 1.5). This cycling of river water into and out of the alluvium

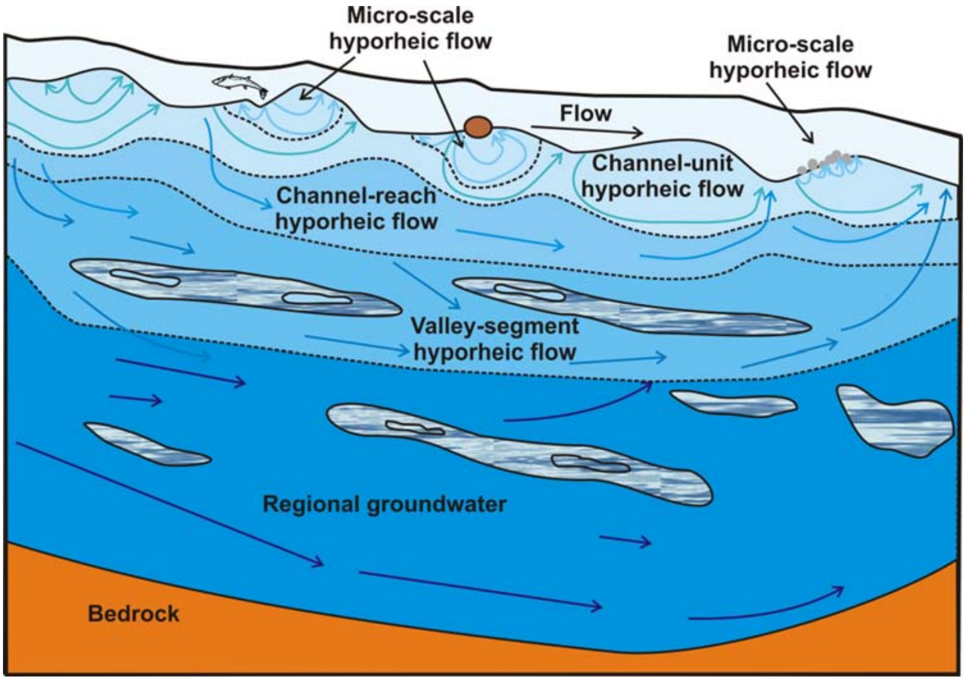


FIGURE 1.5 Five scales of nested flow and exchange between surface and subsurface water for a longitudinal profile along a river valley: (A) microscale circulation (flow paths less than a channel width (*W*) in length) caused by local head variations at the streambed induced by objects in the flow (e.g., large particles, logs, and biotic mounds, such as salmon redds or root boles); (B) channel-unit scale due to streambed head variations around individual bed forms (e.g., dunes, bars, steps) or biotic structures (e.g., beaver dams, log jams), with flow paths up to several *W*; (C) channel-reach scale due to streambed head variations across a sequence of similar channel units (e.g., pool-riffle morphology *sensu* Montgomery & Buffington, 1997), with flow paths of tens of *W*; (D) valley-segment scale driven by head variations from spatial changes in valley confinement (floodplain width), alluvial depth, or underlying bedrock topography, with flow paths of hundreds to thousands of *W* (Edwards, 1998; Baxter and Hauer, 2000; Dent et al., 2001; Malard et al., 2002); and (E) regional groundwater scale driven by head gradients due to overall basin slope and water-table slope, with flow paths $>10^3$ *W*. Horizontally shaded lenses are impervious clay layers that can alter the extent and direction of hyporheic exchange. *Modified from Alley et al. (1999) and Buffington and Tonina (2009b).*

allows mixing with the shallow groundwater, creating physical and biological gradients that structure both surface and subsurface ecosystems, creating complex biogeochemical cycles (Krause et al., 2011). Hyporheic exchange is driven by Darcy's law (1), but the energy head is controlled by conditions within the stream and, in particular, at the streambed surface. As such, the velocity head is no longer negligible when considering hyporheic flow.

In alluvial valleys, surface water and groundwater interact at different spatial and temporal scales that manifest as a hierarchy of nested circulation cells from near-surface hyporheic exchange to deep, regional, groundwater flow (Fig. 1.5). These scales are primarily formed because of different spatial patterns of energy head, some of which may vary temporally

(Tóth, 1963; Boano et al., 2014). Although each scale is idealized as a separate flow path, physical and chemical mixing between circulation cells occurs through numerous processes, including diffusion, advection, dispersion, divergence around heterogeneities of various scales (such as sand and clay lenses), and convergence in upwelling zones (Fig. 1.5).

At the regional scale, groundwater flow depends on (1) the overall water-table slope, (2) water levels in surface water bodies (e.g., rivers, lakes, and wetlands), and (3) characteristics of the porous media (thickness, hydraulic conductivity, heterogeneity) (Winter et al., 1998). At this scale, the water table typically follows topographic relief, but in a subdued way (Tóth, 1963; Wörman et al., 2006), and the river network can be modeled as a series of straight line segments, with energy head varying over length scales of several thousand channel widths (Guevara Ochoa et al., 2020). The water-surface elevation of other water bodies, such as lakes and wetlands, can be treated as constant or varying temporally. Groundwater flow is constrained and modulated by geological features as discussed above. Local perturbations of the energy head (for instance due to a single groundwater pumping well) may have negligible impacts at this scale. Streams can be divided into losing, gaining, or neutral segments. As the spatial scale becomes smaller, topographic features within the river corridor become progressively more important.

At the valley scale, circulation cells are driven not only by head gradients but by spatial changes in alluvial volume and hydraulic conductivity, which can be quantified by expanding the Darcy equation to account for spatial variation of those factors (Tonina and Buffington, 2009b). In particular, valley-scale circulation results from spatial changes in valley confinement (floodplain width), valley slope, geology (rock type), or underlying bedrock topography. Important features are bedrock knickpoints (Wondzell and Swanson, 1996, 1999; Baxter and Hauer, 2000) and large-scale changes in lithology and heterogeneity of alluvial deposits. For example, the frequency of elevation changes in the underlying bedrock topography may structure broad-scale variations in the depth of alluvium that in turn generate valley-scale circulation, with benthic animals congregating at upwelling locations due to relatively stable thermal and discharge regimes (Baxter and Hauer, 2000), although other physical factors may also influence habitat selection (Bean et al., 2014). Furthermore, at this scale, river hydraulics strongly influence the local connectivity between the river and its aquifer via relatively deep hyporheic exchange (Fig. 1.5). Rivers may now be modeled as a curvilinear bend moving through the floodplain, with changes in water-surface elevation and energy head dependent on spatial changes in channel roughness and geometry that can be predicted from one-dimensional hydraulic models (Fleckenstein et al., 2006; Lautz and Siegel, 2006). Sediment transport history also becomes important as buried paleochannels and stratigraphy of the streambed may form preferential hyporheic flow paths within the river valley (Stanford and Ward, 1993).

At the channel-reach scale, the river appears as a collection of repeating sequences of channel units (e.g., step-pool or pool-riffle couplets) (Fig. 1.5), with head gradients structured by the amplitude and wavelength of bed topography, and spatial changes in river depth and slope (Elliott and Brooks, 1997a,b; Kasahara and Wondzell, 2003; Buffington and Tonina, 2009). Hyporheic circulation at this scale is shallower than that of valley-segment scales but can be influenced by similar processes occurring at more local scales. These processes include changes in reach slope, mesoscale changes in the volume of alluvium, cross-valley head differences between the main channel and secondary channels (Kasahara and Wondzell, 2003), and flow through the floodplain (between meander bends (Wroblicky et al., 1998; Cardenas, 2009; Boano et al., 2010) or within buried paleochannels (Stanford and Ward, 1993). Reach-scale hyporheic circulation is also caused by irregularity amongst bed forms, with topographic low points driving larger-scale circulation and capturing hyporheic circulation of upstream channel units (Gooseff et al., 2006). Three-dimensional modeling of groundwater-surface water interaction at this scale may require two-dimensional hydraulic models of water-surface elevations within the stream to properly define both lateral and longitudinal gradients (Benjankar et al., 2016), but constant values also have been used (Storey et al., 2003).

At channel-unit and micro scales, hyporheic circulation is shallow and completely enveloped within larger-scale boundary conditions, because the physical domain is not large enough for interstitial flows to adjust to the local pore conditions, but instead is fully dominated by the boundary conditions (Tonina et al., 2016). Channel-unit circulation is associated with head variations around individual morphologic elements, such as pools and bars (Zarnetske et al., 2011), or biotic structures, such as beaver dams and log jams. In contrast, microscale circulation results from local, small-scale variations in channel characteristics (e.g., variation of the head around individual logs or clusters of streambed particles, or variation of hydraulic conductivity around a buried sand lens within otherwise coarse alluvium). At this scale, nesting and foraging activity of benthic animals also can alter bed topography, grain size, and porosity, thereby inducing and modulating hyporheic circulation (Ziebis et al., 1996; Statzner et al., 1999; Tonina and Buffington, 2009a; Pledger et al., 2017; Sansom et al., 2018). Similarly, aquatic and riparian vegetation can cause hydraulic pressure variations that drive hyporheic circulation and fine-sediment deposition that alters hydraulic conductivity (e.g., Magliozzi et al., 2018). At the microscale, pressure and velocity fluctuations due to turbulence may cause mass exchange between the river flow and near-surface pore water, resulting in hyporheic exchange (Blois et al., 2014; Roche et al., 2019). Because turbulence rapidly decreases within sediment interstices, turbulence exchange is generally limited to a near-surface layer, with thicknesses ranging from 2 to 10 times the median grain size of the streambed sediment (Packman et al., 2004; Detert et al., 2007; Tonina and Buffington, 2007). The turbulence-damping effect of the sediment increases with fine sediment, such that sand-bed streams may have shallow depths of turbulence-induced hyporheic exchange compared to gravel-bed rivers. However, sand-bed rivers are characterized by migrating bedforms at most discharges (Mohrig and Smith, 1996), with bed load transport causing a plug-flow mechanism of hyporheic exchange, known as turn-over (Elliott and Brooks, 1997a,b), in which surface water is trapped within sediment pores during bedform deposition, and released during erosion as the bedform migrates downstream. Consequently, the larger the bedform the deeper the exchange; similarly, the more active the bed load transport the faster the exchange. This mechanism may also occur in braided gravel-bed rivers due to their high rates of movement but is not expected to be important in other coarse-grained rivers, where bedforms are generally immobile except during bankfull flow or larger floods (Montgomery and Buffington, 1997).

# Aquifer function

## Flow and transport in aquifers

Streamlines in a fluid flow as described earlier indicate the main flow direction/path. Mixing of water from different flow paths occurs where those lines converge; for example, at groundwater discharge locations, such as wetlands, springs, and in the vicinity of a well when water is pumped. In addition, temporal variability of mixing processes may occur. For example, seasonality in groundwater recharge causes variability in the mixing of different water from the unsaturated and saturated zone throughout the year (Jasechko et al., 2014). Mixing water from different flow paths can be particularly relevant for geochemical and ecological processes. Water from individual flow paths may have distinct physical, chemical, and biological compositions. When different types of water with different physical and chemical compositions mix, other reactions might be triggered as well. Those mixing processes can create *hot spots* and *hot moments*, where reaction rates are larger compared to surrounding locations or to other time periods (McClain et al., 2003). Mixing is also relevant when pumping a fully screened well, as water from very different flow lines converges at the well (Tonina and Bellin, 2008). Thus, any water sampled at such locations represents the weighted average of fluxes contributing to the sample, which may have a different biogeochemical composition than would otherwise occur at that location in the absence of mixing.

For understanding the physical, chemical, and biological composition of groundwater, general transport processes are important in terms of how they influence the fate of reactive and nonreactive solutes or particles in groundwater. The general transport processes are advection, hydrodynamic dispersion, and diffusion. This applies to both reactive and nonreactive species, with the former also being affected by chemical reactions: dissolution, precipitation, and sorption. Advection is the entrainment of solutes/particles by the groundwater flux along flow paths. In contrast, hydrodynamic dispersion considers the entire distribution of fluid velocities within −microscopically and macroscopically- nonuniform media and the consequent spreading of solutes in both the main flow direction (longitudinal dispersion) and perpendicular to it (transverse dispersion). The ability of a given media to disperse solutes is described in terms of its *dispersivity*, which is an empirical parameter that increases with scale and flow distance (Gelhar et al., 1992).

Whereas hydrodynamic dispersion is a property of the flow field, and thus only relevant in a flowing system, diffusion results in the movement of solutes due to physical and chemical concentration gradients independent of fluid velocity. Because hydrodynamic dispersion and diffusion are often difficult to distinguish, their effects are often combined when modeling solute transport. Spreading due to diffusion becomes more important if fluid velocities are small and/or in the presence of immobile/stagnant water (Knorr and Blodau, 2009). Special behavior is shown by biporous systems, exhibiting large contrasts in permeability. Here, the transport of water is different from solutes, because the solutes diffuse from areas of high permeability into less permeable areas (or *vice versa* as a function of the concentration gradient). This process is of particular importance when considering the transport of pollutants, as these zones can act as long-term stores. Both, hydrodynamic dispersion and diffusion can strongly influence ecosystem services like the degradation of contaminants as they contribute to mass transfer, thus potentially causing mass transfer limitations at various scales (Meckenstock et al., 2015).

The processes described above may be limited by pore size. If particulate matter, either abiotic or biotic (e.g., viruses, bacteria, or groundwater fauna), is larger than a given pore size (Fig. 1.3), the particles simply cannot be transported through the porous media. Therefore, the particulate matter is filtered by the pores and/or is only transported in pores that are larger than the particle size. The former results in the retardation of particulate matter that may clog pores and further reduce transport, while the latter causes accelerated transport through larger pores with faster flow velocity. Thus, the average particle velocity (only transported through the larger pores) may be faster than the average velocity of all water in the system (flow through the entire pore system).

The main retardation process concerning reactive solutes or particles is sorption (i.e., their interaction with the solid phase due to chemical or physical processes). Sorption strongly depends on surface properties and/or properties of the reactant and surrounding water (e.g., ion strength). Sorption can be irreversible (attachment only) or reversible (attachment and detachment). Sorption is an important process for many nutrients and pollutants, but also for viruses and bacteria affecting their fate in groundwater (Tufenkji, 2007). Although pollutants might be immobilized for long periods due to sorption, this is only temporal retardation of transport, not the elimination of the pollutants. Complete elimination of pollutants occurs when they are sufficiently degraded; however, more toxic metabolites can be formed. Pollution can be particularly problematic in karst systems due to the rapid input of pollutants to the groundwater system via fissures, macropores, and tunnels, with relatively less filtration of particulate matter compared to granular porous media.

## Groundwater age

From the flow paths and transport properties along those paths, time scales of flow and transport can be assessed. Those time scales of flow and transport also influence ecosystem processes and water quality because the time since groundwater was recharged is relevant for biogeochemical processes (van der Velde et al., 2010), weathering of minerals (Maher, 2010), degradation of pollutants (Meckenstock et al., 2015), water availability in the critical zone (the area between the vegetation canopy and unweathered subsurface bedrock; Grant and Dietrich, 2017; Sprenger et al., 2019), renewal of groundwater (Jasechko, 2019; Moeck et al., 2020), and estimation of groundwater volume (Gleeson et al., 2011). Thus, those time scales are also used to assess both the intrinsic and specific vulnerability of groundwater bodies (Chatton et al., 2016; Wachniew et al., 2016; Jasechko et al., 2017). A particular concern for human use of aquifers is quantifying renewal times so that groundwater is not overpumped and depleted relative to the time needed to replenish the aquifer; which is a common problem for aquifers containing very old groundwater, indicative of low renewal rates (le Gal La Salle et al., 2001; Favreau et al., 2002; Gonçalvès et al., 2013; Gardner and Heilweil, 2014).

Groundwater age is generally defined as the time elapsed since groundwater entered the subsurface (Bethke and Johnson, 2008). The mean water transit time, sometimes referred to as the turnover time, is defined as the ratio of the mobile water volume to the volumetric flow rate (Kreft and Zuber, 1978). It is the mean time between when water enters and leaves the system, also referred to as the *residence time*. As the mobile water volume is rarely known, tracers in combination with mathematical models are often used to determine the transit times (Maloszewski and Zuber, 1982). However, certain tracers only cover certain ranges of expected water ages (Newman et al., 2006; Suckow, 2014). Further, in the presence of immobile water or for nonideal conditions, the tracer transit time is different from the water transit time because the tracer diffuses into immobile zones and back, thus increasing its transit time relative to water flow (Maloszewski et al., 2004). This complication can be addressed through multi-tracer studies to better understand mixing processes, aquifer functioning, and groundwater age.

Understanding groundwater age and system behavior may also require knowing the distribution of transit and residence times. For example, very different distributions can have similar mean values (Wachniew et al., 2016), creating problems of equifinality. As such, one may need to know the entire distribution of transit and residence times to determine how potential pollutants are diluted or if preferential flow is of relevance. The estimation of mean transit times and transit-time distributions in groundwater has been a challenge for decades; an issue that has been summarized in several different reviews (Suckow, 2014; Turnadge and Smerdon, 2014; McCallum et al., 2015; Cartwright et al., 2017; Jasechko, 2019; Sprenger et al., 2019).

Groundwater ages range from days to weeks for near-surface flow in the variably saturated zone (Ayraud et al., 2008; Le Gal La Salle et al., 2012; Marçais et al., 2018) or during flood events, particularly in karstic systems (Delbart et al., 2014; Palcsu et al., 2021). Such low residence times may be quantified using a variety of tracers (e.g., anthropogenic gases, organic matter, tritium, stable isotopes, and dyes). Groundwater ages rapidly increase with depth, spanning several decades to hundreds of years for both unconfined and confined aquifers, while ages of millions of years have also been determined in sedimentary basins associated with marine environments (Gleeson et al., 2000). Saline and extremely old fluids were also discovered in deep crystalline formations, representing extremely slow regional flow (Bottomley et al., 1994; Aquilina et al., 1997; Greene et al., 2008; Bucher and Stober, 2010) that is controlled by microporosity (Fig. 1.3) (Waber and Smellie, 2008; Aquilina and Dreuzy, 2011; Aquilina et al., 2015). Radioactive or accumulative tracers ($^{14}C$, $^{4}He$, $^{36}Cl$, $^{39}Ar$, $^{40}Ar$, $^{81}Kr$, $^{129}I$) were used to characterize these old ages. Although relationships to surface and nutrient fluxes are extremely limited, these deep aquifers constitute ecosystems with specific microbial communities (Pedersen, 1997; Hallbeck and Pedersen, 2008).

## Modeling aquifers

Groundwater flow in aquifers is typically more complex than what is shown in Fig. 1.1. Complex aquifers require comprehensive definitions of the geologic features of each rock type within an aquifer to correctly parameterize spatial variation of hydraulic conductivity. However, the degree of heterogeneity and the morphologic distribution of different rock/sediment facies is usually unknown. Nevertheless, establishing a model of the aquifer remains a useful tool for analyzing factors such as groundwater flow patterns, human uses of the resource, and transport properties of nutrients and pollutants. Approaches for modeling groundwater can be broadly divided into spatially-distributed vs. lumped-parameter models. The former typically employs finite analyses, in which the aquifer is divided into small cells with distributed hydrogeological properties (e.g., MODFLOW; Langevin et al., 2017). These properties allow the flow and transport of material, along with their spatial variation, to be computed. Numerous other models exist that allow implementation of various hydrological and chemical processes, as well as coupling between surface and subsurface systems (e.g., PLFOTRAN (Hammond et al., 2012) and HydroGeoSphere (Therrien et al., 2010). Because the spatial distribution of hydraulic properties within the aquifer is typically unknown, they can be characterized as stochastic variables, producing a number of possible realizations. This is especially important for solute transport, where the fate of the solute is studied using a Monte Carlo approach in which many different realizations of hydraulic properties are generated, from which the solute transport and associated transformations are then studied statistically. "Black box" or lumped-parameter models have also been used to determine simple characteristics, such as groundwater flow or mean residence time (Małoszewski and Zuber, 1985). The simplest one is the piston-flow model, which describes the aquifer as a "tube" (Fig. 1.6A). The simple interpretation of groundwater "age" (discussed in the previous section) refers to this type of model. A more representative lumped-parameter model is the exponential approach, which integrates an infinity of flow lines along a vertical axis, with an exponentially decreasing proportion of flow lines with depth and age (Fig. 1.6B). The third type of lumped-parameter model, which characterizes conditions often observed in natural environments, is the binary mixing model (Fig. 1.6C). This model considers mixing between two water bodies, a modern component (which may be young recharge water or relatively recent groundwater) and an older component (which might be defined as containing no chlorofluorocarbons (CFCs, used as a tracer) or simply as older than the modern component).

A variety of models also have been developed for different scales of hyporheic exchange that elucidate different hydraulic environments and their consequences for fauna and water quality (further discussed by Tonina and Buffington, this volume). Although hyporheic and groundwater models employ similar mechanics related to Darcy's law, the coupling of the two is frequently uneven. For example, some studies combine complex hyporheic models with simplified groundwater flow (e.g., Boano et al., 2008; Marzadri et al., 2016), while others use complex groundwater models with simplified hyporheic flow (e.g., Therrien et al., 2010) that do not fully capture the various scales of flow and interaction illustrated in Fig. 1.5 without using high-resolution topography and a fine-scale numerical mesh. Recent modeling approaches use artificial intelligence, such as machine learning or neural networks, which are particularly promising for investigating heterogeneous and complex aquifers.

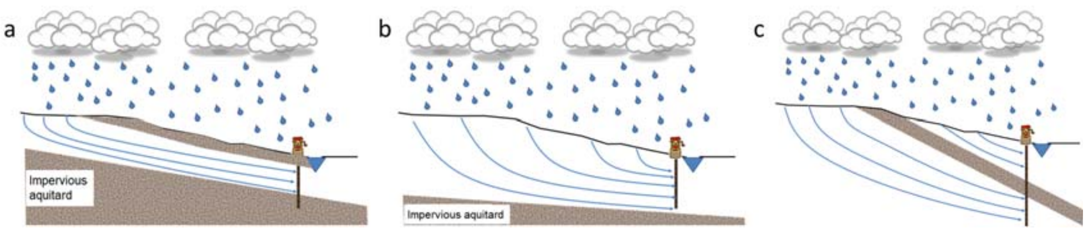


**FIGURE 1.6** Lumped parameter models of aquifers: (A) piston flow model, (B) exponential model, and (C) binary mixing model. *Original drawing from Condate-Eau laboratory, used with permission.*

# The chemical composition of groundwater

## Origin of chemical compounds in surface waters

Groundwater derives its chemical composition initially from seawater through the integration of sea spray in vapor fluxes that give birth to clouds. Precipitation thus contains chemical elements that derive mainly from seawater. Seawater influence is maximized in coastal areas, with chloride (Cl) concentration (the major ion in seawater) ranging from 15 to 25 mg/L. A few kilometers inland, this concentration rapidly decreases toward $<10$ mg/L. Further inland, especially in mountainous areas, Cl concentration in precipitation is only a few mg/L.

For a chemical element *X*, the seawater contribution may be calculated in terms of the chloride concentration:

$$X_{sw} = (Clsw \times Xsp)/Clsp(x) \tag{1.2}$$

where the *sw* and *sp* subscripts refer to seawater and the sample, respectively, and *x* is the proportion of the chemical component *X* in the sample. A concentration higher than the marine contribution indicates another source, which might be derived either from mineral dust dissolution or from gaseous anthropogenic inputs. The composition of precipitation undergoes further chemical evolution in the soil. First, plant transpiration and, in high-temperature areas, evaporation, linked together as evapotranspiration (ETP), are responsible for the loss of a large amount of water to the atmosphere. In temperate areas, ETP leads to the loss of about half of the initial water content, thus doubling the chemical concentration. When ETP is higher, concentration may be multiplied by a factor of 3 to 4, further leading to evaporates and brines in specific environments. While ETP can concentrate all chemical elements, other processes in the soil can substantially modify the chemical composition. A major driver of the chemical reactivity of water in soils is related to the acidity of water. Precipitation contains dissolved $CO_2$ after equilibration with the atmosphere and contains about 0.5 mg/L bicarbonate ($HCO_3^-$) at 25°C. As $HCO_3^-$ concentration in groundwater is usually several tens of milligrams, the majority of $CO_2$ is related to organic matter degradation within the soil. Water acidity makes groundwater in the unsaturated zone or in the variably saturated zone highly reactive. The most easily soluble mineral that may account for this acidity is calcite ($CaCO_3$). Calcite is present in various proportions of sedimentary rocks, but is also present even in metamorphic or igneous rocks such as granites (White et al., 1999), thus making it ubiquitous at the earth's surface. This results in the dominance of $HCO_3^-$ and calcium ion ($Ca^{2+}$) concentrations in surface water and shallow groundwater.

A second chemical process that also strongly modifies the chemical composition of water that enters the unsaturated zone is exchange with clays. Clay minerals are made of layers with negative electrical charges. These negative charges are balanced by cations located in between the layers. These cations are likely to move out of the minerals if another cation is available to replace them. These cations constitute a pool contained in the soil that is termed the cation exchange capacity (CEC) of the soil. The CEC directly contributes to the cationic composition of water in the soil and strongly increases, with ETP, the overall concentration of cations in water.

## Water—rock interactions within aquifers

Precipitation enters the soil and migrates toward the saturated zone during recharge, increasing the total solute concentration in water, which progressively shifts the original composition from seawater ratios toward mineral-source ratios, especially for cations. Once at the top of the saturated zone, recharging water joins the groundwater flow lines and atmospheric exchanges stop, especially for gas exchange, which controls, for example, oxygen concentrations. While water moves downward, it crosses the weathered zone and reaches the transition to the unweathered zone. Water, which is chemically aggressive is the most reactive when it first encounters fresh minerals, which tend to dissolve. Mineral dissolution decreases the chemical reactivity and weathering appears as a front that slowly moves downward.

In competent bedrock, groundwater flows slowly along mineral facets in pores and microfractures of the aquifer, where water—rock interaction may also modify the groundwater composition. Most minerals are less reactive than calcite; however, the long groundwater residence time, from years to tens or even hundreds of years in some cases, allows for water and minerals to evolve toward equilibria. In hard-rock aquifers, water—rock interaction is dominated by silicate weathering of minerals such as alkali and plagioclase feldspars, which provide potassium, calcium, and sodium ions ($K^+$, $Ca^{2+}$, and $Na^+$) and silicon dioxide ($SiO_2$). Quartz is also a source of silica. In limestones, the dissolution of magnesium carbonates ($MgCO_3$) occurs with increasing residence time and follows calcite dissolution. Magnesium carbonate dissolution, in turn, induces calcite precipitation, providing typically decreasing ratios of Ca/Mg (Back et al., 1983). However, dissolution processes are fairly complex at the various spatial and temporal scales of the critical zone (Andrews et al., 2011; Brooks et al., 2015), even in carbonate aquifers. In addition to groundwater dissolution, carbon evolves during river transport toward the ocean (Hotchkiss et al., 2015; Ward et al., 2017). Weathering is also highly sensitive to human activities (Macpherson, 2009; Aquilina et al., 2012a).

Protons ($H^+$) promote mineral dissolution through acid-base reactions. Oxygen ($O_2$) also enhances mineral dissolution through redox reactions. It reacts with iron-rich minerals such as biotite. The spatial and vertical stratification of redox reactivity is similar to that of acid-base processes described above.

## Major water quality types

Surface water and groundwater are characterized by their chemical composition, with major components commonly used for the classification of different water types, such as calcium bicarbonate types or sodium chloride types. Piper ternary diagrams are used to plot groundwater composition for classifying different chemical types of water. Within Piper diagrams, water samples are represented as a point defined by the weight of chemical components (e.g., $Cl^-$, $SO_4^{2-}$, $HCO_3^-$) expressed as a percentage of the total concentration of anions or cations. The value of this approach is that it allows one to easily compare groundwater having different total concentrations. However, identifying slight seawater contamination (a few percent or less) is difficult in Piper diagrams. It is also difficult to identify in standard bivariate plots showing relative compositions because seawater is several orders of magnitude more concentrated than typical groundwater. Piper diagrams are more amenable to such analyses when seawater or any other water types are used as endmembers for comparison with groundwater samples. Piper diagrams are thus useful to determine water groups and the potential mixing of different water types. Statistical tools such as hierarchical classification more precisely help to define groups within water samples. Furthermore, as Piper diagrams only show element proportions, they are not adequate tools to elucidate or describe biogeochemical processes, which should be more precisely quantified in bivariate plots or other analyses that allow specific quantification of reactions. For example, bivariate plots of Ca, Mg, or Ca/Mg versus $HCO_3$ may quantify carbonate reactions (dissolution and/or precipitation, which might on some occasions be coupled), or Na−Cl, which may distinguish ETP enrichments with seawater Na/Cl molar ratios (0.8) from halite dissolution (1/1). More complex processes for trace elements may be solved using phase diagrams.

## Reduced environments

While acid-base reactions dominate cation processes, redox processes might influence both anion concentrations and trace elements, especially metals. Acid-base reactions represent the exchange of protons, while redox reactions represent an exchange of electrons. Redox reactions in groundwater environments require an abundance of electron acceptors, such as oxygen, nitrate, sulfate, and electron donors, such as natural organic matter. The element cycling of oxygen and nitrogen is specifically presented below. Sulfur represents a specific case as it is a constituent of many minerals in the environment, and depending on redox reactions, can bind or release metals, such as iron. Sulfur is present in both marine and continental environments, especially in the form of sulphate. It is introduced in marine sediments or lake sediments and might precipitate in reducing conditions below the seafloor or lake floor in the form of pyrite. Sulfur is also present in igneous rocks and metallic sulfur, such as pyrite, is ubiquitous in geological formations.

Metallic sulfur that has been formed in deep reducing environments, either sedimentary or igneous, is highly reactive in the surface environment, where it is rapidly oxidized by dissolved oxygen. Pyrite constitutes a source of iron, but several metals (e.g., As, Co, Zn, Au) are also associated with iron and may be released through pyrite dissolution. Furthermore, other metallic sulfur species may also be present locally and represent a major metal source.

Whether aquifers are oxic or anoxic depends on the availability of dissolved oxygen. If the reactivity of the system is low (e.g., as a consequence of lacking electron donors or slow reaction rates) or if enough dissolved oxygen is replenished (e.g., by gaseous exchange with the atmosphere or with new water entering the system), oxic conditions may prevail. In contrast, if dissolved oxygen is absent due to consumption or lack of replenishment, anoxic conditions establish. The common perception is that shallow subsurface environments are oxic, while confined and/or deep aquifers are reducing environments. However, even in unconfined and shallow water-table aquifers, reducing conditions can develop as a function of flow path length and slowing of groundwater flow velocity or due to the abundance of electron donors (i.e., related to the mineralogy of the geological formation of the aquifer). Reducing environments are characterized by low or negative redox potentials, also known as oxidation/reduction potentials that are measured (e.g., with an $E_h$ meter that measures electrical potential in millivolts) by low oxygen concentrations. Indeed, oxygen is the most well-known driver of redox potential although other components also contribute to the redox processes and control the redox potential (Stumm and Morgan, 1996). Groundwater exploitation and distribution result in mixing processes as explained above. Such mixing may induce reactive processes as reduced groundwater with no oxygen and high metal content mixes with surface groundwater with high oxygen or nitrate concentrations. These interactions produce metal precipitation, which has been identified as a major problem in groundwater well production (Williams and Oostrom, 2000; Burté et al., 2019).

## Chemical and nutrient fluxes in aquifers

### Biogeochemical reactions

Microorganisms obtain their energy from chemical reactions. Breaking nuclear bonds provides energy that is used to sustain various metabolic processes and bacterial growth. Several reactions are used depending on the redox environment, which is directly related to the nutrients available. A succession of microbial reactions has been described (Fig. 1.7) from gaining either the most or least energy out of a reaction. Oxygen reduction in combination to the oxidation of an organic or inorganic electron donor produces a high energy level. Nitrate reduction also produces a great deal of energy, although less than oxygen reduction, which partly explains that nitrate reduction appears only in low-oxygen environments. Sulfate

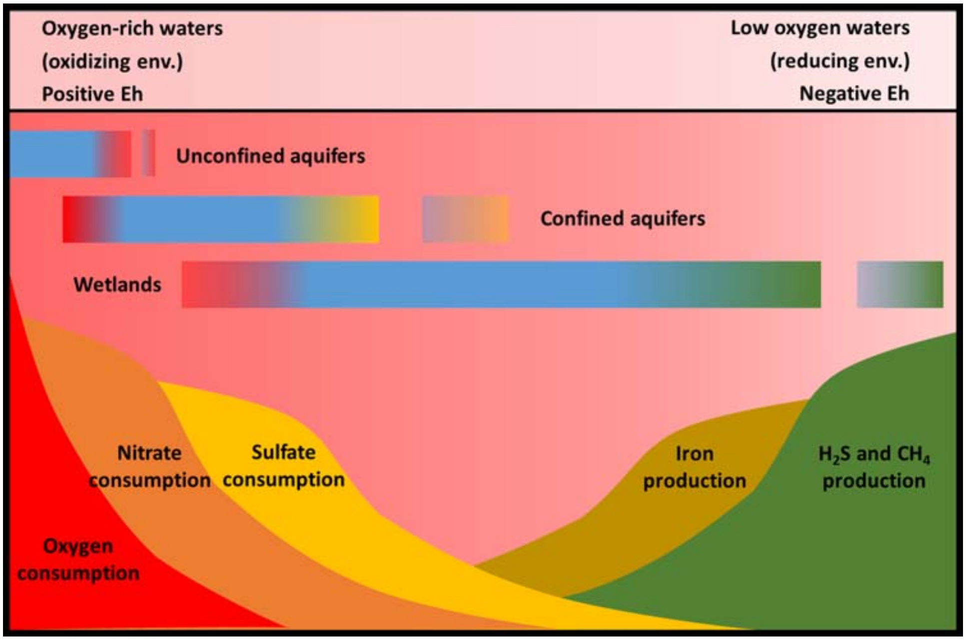


FIGURE 1.7 Succession of biogeochemical reactions in a redox gradient.

reduction to hydrogen sulfide ($H_2S$) is characteristic of highly reducing environments as well as methane production, which appears as the most reducing reaction. This succession may be observed and modeled in a variety of reduced environments, such as peatlands, along groundwater flow paths that can vary in length from a few centimeters to hundreds of meters (Hunter et al., 1998; Rezanezhad et al., 2016).

## Oxygen in groundwater

Oxygen is present in all surface water because of its interaction with atmospheric oxygen. However, oxygen supply may be limited to near-surface layers for stratified water bodies. Equilibria between water and the atmosphere for a given gas are described by Henry's law, which defines gas solubility:

$$P_E = X_E \times K_{HES} \tag{1.3}$$

where $P_E$ is the partial pressure of gas $E$ in the air equilibrated with the solution $S$, $X_E$ the molar fraction of $E$ in solution, and $K_{H\ E,S}$ the Henry's constant of $E$ in solution $S$ at a given temperature and pressure.

Solubility is specific to each gas and varies with both temperature and pressure. However, for a given temperature and pressure, an atmospheric increase leads to a dissolved concentration increase. This is the case for the $CO_2$ increase in the atmosphere during the 20th century, which has led to oceanic acidification. Gas solubility increases with decreasing temperature, and recharge in cold areas (below 10°C) allows oxygen concentrations equal to or slightly above 10 mg/L. This concentration decreases to 8−6 mg/L for recharge temperatures higher than 15−20°C.

Below the groundwater−atmosphere interface, oxygen is consumed by microorganisms through respiration. In unconfined aquifers, oxygen concentration decreases vertically over length scales of several tens of meters. Even though this represents a relatively shallow depth, the residence time may reach 10−20 yrs, which defines an oxygen consumption rate. The lower part of aquifers, with thickness greater than several tens of meters, may thus present hypoxic and reduced environments, with low to almost no oxygen available. While the above is generally true, the oxygen distribution also depends on the reactivity and availability of electron donors, as well as the distribution of flow lines. Recharge zones may be strongly oxic even below the surface, while confined areas with low oxygen concentration can be encountered at shallow depths (Hose et al., 2000; Röling et al., 2001; Maamar et al., 2015).

Beyond such stratification of oxygen concentrations, oxygen mixing zones may constitute hotspots of reactivity. This occurs in the hyporheic zone, where low-oxygen groundwater mixes with oxygenated river water within the streambed sediments. Within heterogeneous aquifers, fractures may transport fresh groundwater with high oxygen concentrations to depths of several tens or hundreds of meters. This leads to important mixing processes that may drive microbial reactions as observed for iron oxidizers (Bochet et al., 2020).

Peatlands and moors also constitute areas where oxygen distribution may be highly heterogeneous, with gas distributed throughout the whole environment (Rosenberry et al., 2006). This distribution reflects the development of microsites of microbial activity within the peat (Nunes et al., 2015), with specific microbial habitats adapted to reduced conditions. These areas also constitute hot moments with periods of water renewal, oxygen and nutrient fluxes, and periods of reducing conditions. Following such periods, which are characterized by peat desiccation, peat rehumectation leads to the oxidation of organic matter and/or pyrite. Such oxidation induces acid pulses with high sulfate concentrations (Mitchell and Branfireun, 2005; Knorr and Blodau, 2009).

## Nitrogen and emerging contaminants in groundwater

While biological processes are key in nitrogen cycling in the environment, human activities have significantly modified the nitrogen cycle by converting huge amounts of atmospheric nitrogen to mineral fertilizers through the Haber-Bosch process (Erisman et al., 2011). Fertilizers, and with them the so-called green revolution, have led to intensive agriculture development in many parts of the world and an increase in both organic and inorganic nitrogen use (Ågren and Bosatta, 1988; Alvarez-Cobelas et al., 2008). The consequence of this development is massive nitrate pollution of surface waters that started in the 1970s and has increased through the end of the 20th century. Environmental regulations and public pressure have led to modifications of agricultural practices and decreasing nitrate concentrations in rivers during the last few decades, although the problem is still ongoing. According to the definition of planetary boundaries (i.e., environmental boundaries that define a habitable planet), nitrogen is one of the limits that anthropogenic activities have crossed (Steffen et al., 2015).

While agricultural activities have applied nitrogen fertilizers to the soil surface, N-compounds (organically bound N, ammonium, nitrite, and nitrate) have progressively entered recharge fluxes and have contaminated groundwater. Within such aquifers, a nitrogen reservoir exists that is a legacy of past agricultural practices that contributes to nitrate concentrations in rivers several years and decades after the application of surface fertilizers. This situation makes political decisions and environmental constraints challenging because it is difficult to disentangle current versus historic effects, and because time lags are often ignored in groundwater resources management (Aquilina et al., 2012b; Stumpp et al., 2016; Wachniew et al., 2016). Nitrate may accumulate at a slower rate in the lower parts of aquifers because of autotrophic denitrification reactions (Rivett et al., 2008). Once oxygen has been consumed, nitrate becomes the most energetically favorable electron acceptor, and various groups of microorganisms are able to reduce nitrate to dinitrogen or intermediate products, such as nitrite or nitrous oxide.

Beyond nitrogen, an extremely wide range of contaminants is related to human activities. In particular, a large number of inorganic and organic molecules have been introduced to the environment through human use of pesticides and pharmaceuticals. These contaminants are also transferred to groundwater through various soil processes (Jury and Wang, 2000; Arias-Estévez et al., 2008; Teuten et al., 2009). The extremely high number of introduced contaminants represents a major issue, as due to the generally low concentrations, many constituent molecules are not degraded by microbes nor easily detected by the analytical protocols available (Gavrilescu et al., 2015). Although pesticides are usually less concentrated in groundwater than in surface water, their degradation products (metabolites) are more prevalent in groundwater, making aquifers particularly vulnerable to such contaminants (Heberer, 2002; Lapworth et al., 2012). Other human activities have introduced a vast of new contaminants in the last few decades, termed *emerging contaminants*, such as endocrine-disrupting compounds, algal toxins, and nanoplastics. Organic contaminants and pathogens are also introduced to the aquatic environment through wastewater, which can lead to groundwater transfer of such contaminants (Nikolaou et al., 2007; Pandey et al., 2014; Bradford and Harvey, 2017).

## Conclusion

Groundwater represents the invisible part of the water cycle due to its subsurface nature. Aquifers occur in a broad range of geological formations, creating diverse physical properties and aquatic environments. Key physical characteristics of these geological formations are their ability to let groundwater flow (permeability), which in turn depends on the extent and connectivity of voids (porosity) within the geological formation, controlling aquifer function. Although the physical structure of aquifers varies between geological formations, most aquifers present a high degree of physical and chemical heterogeneity. This is particularly the case for fractured bedrock and karstic aquifers, which are characterized by two contrasting degrees of permeability: a highly-permeable system comprised of large fracture zones and tunnels, and a much less permeable system within the surrounding matrix of the geological formation. These hydraulic properties and boundary conditions define how fast water moves through the system and the age of the groundwater, which is an important variable for characterizing groundwater functioning and system dynamics.

Although groundwater aquifers are subsurface systems, they are intimately linked to surface water bodies, further enhancing the diversity of the hydrologic system. Depending on topography and local hydraulic gradients, groundwater may upwell into surface environments (springs, rivers, lakes, wetlands) in some locations, while in other parts of a basin, the aquifer will be recharged by surface water through processes of soil infiltration on hillslopes, hyporheic downwelling in rivers, and direct descent of water through surface fractures and inlets in karst terrain. The linkage between surface and subsurface systems and the hydraulic gradients that move water between the two allows for a broad range of physicochemical reactions and biogeochemical processes, emphasizing the need to better integrate disciplines of hydrogeology and ecology (Hancock et al., 2009).

Characterization of aquifer properties and heterogeneities is further used to parameterize aquifer models. Such models range from simple lumped-parameter approaches that represent the ensemble function of the aquifer to spatially-distributed models that reproduce the physical details of groundwater flow and transport. These models can provide important insight regarding system behavior. Quantifying the physical processes and characteristics of groundwater systems through such models also forms the basis for understanding the distribution and activity of living organisms in groundwater environments. In many aspects, the structural features of aquifers, through their control of groundwater flow, set the scene for the diversity and evolution of life in groundwater systems.

Aquifer dynamics and linkages to surface systems also control groundwater quality, which is influenced by processes occurring over multiple spatial and temporal scales. Close to the surface and over short time scales, groundwater quality is affected by the reactivity of rainwater percolating through various types of soil. Below the soil layer, the consumption of various electron acceptors (e.g., oxygen and nitrate) results in chemical reactions that progressively modify water quality through water—rock interactions. All of these processes depend on physicochemical conditions (acidity and redox conditions) that vary along groundwater flow lines. Biological processes additionally modulate chemical conditions, playing a critical role in the cycling of carbon, oxygen, and nutrients. Groundwater quality thus depends on abiotic processes related to soil/rock characteristics and biogeochemical reactions, as well as their interactions. Furthermore, human activities have strongly altered groundwater quality in many parts of the world, especially with the introduction of high nitrogen inputs to ecosystems, but also through the production and use of chemicals. The linkage between surface and subsurface systems, and the fact that aquifers are long-term reservoirs in which contaminants can concentrate, make groundwater quality a major concern, particularly in regions where communities rely on groundwater resources.

From the processes summarized in this chapter, it is clear that there is a need for better integration of hydrogeology, microbiology and ecology to facilitate "the study of interactions between the hydrology of all groundwater bodies and their ecological components" (e.g., Hancock et al., 2009). In this regard, a particularly important area for future research is the documentation of relationships between physical and biological parameters.

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## References

Abbott, B.W., Bishop, K., Zarnetske, J.P., Minaudo, C., Chapin, F.S., Krause, S., Hannah, D.M., Conner, L., Ellison, D., Godsey, S.E., Plont, S., Marçais, J., Kolbe, T., Huebner, A., Frei, R.J., Hampton, T., Gu, S., Buhman, M., Sara Sayedi, S., Ursache, O., Chapin, M., Henderson, K.D., Pinay, G., 2019. Human domination of the global water cycle absent from depictions and perceptions. Nature Geoscience 12, 533—540. https://doi.org/10.1038/s41561-019-0374-y.

Ågren, G.I., Bosatta, E., 1988. Nitrogen saturation of terrestrial ecosystems. Environmental Pollution 54, 185—197. https://doi.org/10.1016/0269-7491(88)90111-X.

Alexander, R.B., Boyer, E.W., Smith, R.A., Schwarz, G.E., Moore, R.B., 2007. The role of headwater streams in downstream water quality. Journal of the American Water Resources Association 43, 41—59. https://doi.org/10.1111/j.1752-1688.2007.00005.x.

Alley, W.M., Reilly, T.E., Franke, O.L., 1999. Sustainability of ground-water resources. US Geological Survey, Circular 1186, Denver, CO.

Alvarez-Cobelas, M., Angeler, D.G., Sánchez-Carrillo, S., 2008. Export of nitrogen from catchments: a worldwide analysis. Environmental Pollution 156, 261—269. https://doi.org/10.1016/j.envpol.2008.02.016.

Amanambu, A.C., Obarein, O.A., Mossa, J., Li, L., Ayeni, S.S., Balogun, O., Oyebamiji, A., Ochege, F.U., 2020. Groundwater system and climate change: present status and future considerations. Journal of Hydrology 589, 125163. https://doi.org/10.1016/j.jhydrol.2020.125163.

Andrews, D.M., Lin, H., Zhu, Q., Jin, L., Brantley, S.L., 2011. Hot spots and hot moments of dissolved organic carbon export and soil organic carbon storage in the Shale Hills catchment. Vadose Zone Journal 10, 943—954. https://doi.org/10.2136/VZJ2010.0149.

Aquilina, L., Dreuzy, J.-R. De, 2011. Relationship of present saline fluid with paleomigration of basinal brines at the basement/sediment interface (Southeast basin—France). Applied Geochemistry 26, 1933—1945. https://doi.org/10.1016/j.apgeochem.2011.06.022.

Aquilina, L., Ladouche, B., Dörfliger, N., 2006. Water storage and transfer in the epikarst of karstic systems during high flow periods. Journal of Hydrology 327, 472—485. https://doi.org/10.1016/j.jhydrol.2005.11.054.

Aquilina, L., Pauwels, H., Genter, A., Fouillac, C., 1997. Water-rock interaction processes in the Triassic sandstone and the granitic basement of the Rhine Graben: geochemical investigation of a geothermal reservoir. Geochimica et Cosmochimica Acta 61, 4281−4295. https://doi.org/10.1016/S0016-7037(97)00243-3.

Aquilina, L., Poszwa, A., Walter, C., Vergnaud, V., Pierson-Wickmann, A.-C., Ruiz, L., 2012a. Long-term effects of high nitrogen loads on cation and carbon riverine export in agricultural catchments. Environmental Science and Technology 46 (17), 9447−9455. https://doi.org/10.1021/es301715t.

Aquilina, L., Vergnaud-Ayraud, V., Labasque, T., Bour, O., Molénat, J., Ruiz, L., de Montety, V., De Ridder, J., Roques, C., Longuevergne, L., 2012b. Nitrate dynamics in agricultural catchments deduced from groundwater dating and long-term nitrate monitoring in surface- and groundwaters. Science of the Total Environment 435−436, 167−178. https://doi.org/10.1016/j.scitotenv.2012.06.028.

Aquilina, L., Vergnaud-Ayraud, V., Les Landes, A.A., Pauwels, H., Davy, P., Pételet-Giraud, E., Labasque, T., Roques, C., Chatton, E., Bour, O., Ben Maamar, S., Dufresne, A., Khaska, M., La Salle, C.L.G., Barbecot, F., 2015. Impact of climate changes during the last 5 million years on groundwater in basement aquifers. Scientific Reports 5, 14132. https://doi.org/10.1038/srep14132.

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agriculture, Ecosystems & Environment 123, 247−260. https://doi.org/10.1016/J.AGEE.2007.07.011.

Ayraud, V., Aquilina, L., Labasque, T., Pauwels, H., Molenat, J., Pierson-Wickmann, A.C., Durand, V., Bour, O., Tarits, C., Le Corre, P., Fourre, E., Merot, P., Davy, P., 2008. Compartmentalization of physical and chemical properties in hard-rock aquifers deduced from chemical and groundwater age analyses. Applied Geochemistry 23, 2686−2707.

Back, W., Hanshaw, B.B., Plummer, L.N., Rahn, P.H., Rightmire, C.T., Rubin, M., 1983. Process and rate of dedolomitization: mass transfer and $^{14}C$ dating in a regional carbonate aquifer. The Geological Society of America Bulletin 94, 1415−1429. https://doi.org/10.1130/0016-7606(1983)94<1415:parodm>2.0.co;2.

Bailly-Comte, V., Martin, J.B., Screaton, E.J., 2011. Time variant cross correlation to assess residence time of water and implication for hydraulics of a sink-rise karst system. Water Resources Research 47, W05547. https://doi.org/10.1029/2010WR009613.

Baxter, C.V., Hauer, F.R., 2000. Geomorphology, hyporheic exchange, and selection of spawning habitat by bull trout (*Salvelinus confluentus*). Canadian Journal of Fisheries and Aquatic Sciences 57, 1470−1481.

Bean, J.R., Wilcox, A.C., Woessner, W.W., Muhlfeld, C.C., 2014. Multiscale hydrogeomorphic influences on bull trout (*Salvelinus confluentus*) spawning habitat. Canadian Journal of Fisheries and Aquatic Sciences 72, 514−526. https://doi.org/10.1139/cjfas-2013-0534.

Benjankar, R., Tonina, D., Marzadri, A., McKean, J., Isaak, D.J., 2016. Effects of habitat quality and ambient hyporheic flows on salmon spawning site selection. Journal of Geophysical Research: Biogeosciences 121, 1222−1235. https://doi.org/10.1002/2015JG003079.

Bethke, C.M., Johnson, T.M., 2008. Groundwater age and groundwater age dating. Annual Review of Earth and Planetary Sciences 36, 121−152. https://doi.org/10.1146/annurev.earth.36.031207.124210.

Blois, G., Best, J.L., Sambrook Smith, G.H., Hardy, R.J., 2014. Effect of bed permeability and hyporheic flow on turbulent flow over bed forms. Geophysical Research Letters 41, 6435−6442.

Boano, F., Camporeale, C., Revelli, R., 2010. A linear model for the coupled surface-subsurface flow in a meandering stream. Water Resources Research 46, W07535.

Boano, F., Harvey, J.W., Marion, A., Packman, A.I., Revelli, R., Ridolfi, L., Wörman, A., 2014. Hyporheic flow and transport processes: mechanisms, models, and biogeochemical implications. Reviews of Geophysics 52, 603−679.

Boano, F., Revelli, R., Ridolfi, L., 2008. Reduction of the hyporheic zone volume due to the stream-aquifer interaction. Geophysical Research Letters 35, L09401. https://doi.org/10.1029/2008GL033554.

Bochet, O., Bethencourt, L., Dufresne, A., Farasin, J., Pédrot, M., Labasque, T., Chatton, E., Lavenant, N., Petton, C., Abbott, B.W., Aquilina, L., Le Borgne, T., 2020. Iron-oxidizer hotspots formed by intermittent oxic−anoxic fluid mixing in fractured rocks. Nature Geoscience 13, 149−155. https://doi.org/10.1038/s41561-019-0509-1.

Bottomley, D.J., Gregoire, D.C., Raven, K.G., 1994. Saline groundwaters and brines in the Canadian shield: geochemical and isotopic evidence for a residual evaporite brine component. Geochimica et Cosmochimica Acta 5, 1483−1498.

Bradford, S.A., Harvey, R.W., 2017. Future research needs involving pathogens in groundwater. Hydrogeology Journal 25, 931−938. https://doi.org/10.1007/S10040-016-1501-0.

Brooks, P.D., Chorover, J., Fan, Y., Godsey, S.E., Maxwell, R.M., McNamara, J.P., Tague, C., 2015. Hydrological partitioning in the critical zone: recent advances and opportunities for developing transferable understanding of water cycle dynamics. Water Resources Research 51, 6973–6987. https://doi.org/10.1002/2015WR017039.

Bucher, K., Stober, I., 2010. Fluids in the upper continental crust. Geofluids 10, 241–253. https://doi.org/10.1111/j.1468-8123.2010.00279.x.

Buffington, J.M., Tonina, D., 2009. Hyporheic exchange in mountain rivers II: effects of channel morphology on mechanics, scales, and rates of exchange. Geography Compass 3 (3), 1038–1062. https://doi.org/10.1111/j.1749-8198.2009.00225.x.

Burté, L., Cravotta, C.A., Bethencourt, L., Farasin, J., Pédrot, M., Dufresne, A., Gérard, M.F., Baranger, C., Le Borgne, T., Aquilina, L., 2019. Kinetic study on clogging of a geothermal pumping well triggered by mixing-induced biogeochemical reactions. Environmental Science and Technology 53, 5848–5857. https://doi.org/10.1021/acs.est.9b00453.

Cardenas, M.B., 2009. A model for lateral hyporheic flow based on valley slope and channel sinuosity. Water Resources Research 45, 1–5. https://doi.org/10.1029/2008WR007442.

Cartwright, I., Cendón, D., Currell, M., Meredith, K., 2017. A review of radioactive isotopes and other residence time tracers in understanding groundwater recharge: possibilities, challenges, and limitations. Journal of Hydrology 555, 797–811. https://doi.org/10.1016/j.jhydrol.2017.10.053.

Chapelle, F.H., 2001. Ground-Water Microbiology and Geochemistry, 2nd. Wiley, New York, NY.

Chatton, E., Aquilina, L., Pételet-Giraud, E., Cary, L., Bertrand, G., Labasque, T., Hirata, R., Martins, V., Montenegro, S., Vergnaud, V., Aurouet, A., Kloppmann, W., Pauwels, 2016. Glacial recharge, salinisation and anthropogenic contamination in the coastal aquifers of Recife (Brazil). Science of the Total Environment 569-570, 1114–1125. https://doi.org/10.1016/j.scitotenv.2016.06.180.

Crutzen, P.J., 2002. Geology of mankind. Nature 415, 23. https://doi.org/10.1038/415023A.

Darcy, H., 1856. Les fontaines publiques de la ville de Dijon. Libraire des Corps Imperiaux des Ponts et Chaussées et des Mines, Paris.

Delbart, C., Barbecot, F., Valdes, D., Tognelli, A., Fourre, E., Purtschert, R., Couchoux, L., Jean-Baptiste, P., 2014. Investigation of young water inflow in karst aquifers using SF6-CFC-3H/He-85Kr-39Ar and stable isotope components. Applied Geochemistry 50, 164–176. https://doi.org/10.1016/J.APGEOCHEM.2014.01.011.

Dent, C.L., Grimm, N.B., Fisher, S.G., 2001. Multiscale effects of surface-subsurface exchange on stream water nutrient concentrations. Journal of the North American Benthological Society 20 (2), 162–181.

Detert, M., Klar, M., Wenka, T., Jirka, G.H., 2007. Pressure- and velocity-measurements above and within a porous gravel bed at the threshold of stability. In: Habersack, H., Piégay, H., Rinaldi, M. (Eds.), Gravel-Bed Rivers VI: From Process Understanding to River Restoration. Elsevier, Amsterdam, The Netherlands, pp. 85–105.

Dewandel, B., Lachassagne, P., Wyns, R., Maréchal, J.C., Krishnamurthy, N.S., 2006. A generalized 3-D geological and hydrogeological conceptual model of granite aquifers controlled by single or multiphase weathering. Journal of Hydrology 330, 260–284. https://doi.org/10.1016/j.jhydrol.2006.03.026.

Edwards, R.T., 1998. The hyporheic zone. In: Naiman, R.J., Bilby, R.E. (Eds.), River Ecology and Management: Lessons From the Pacific Coastal Ecoregion. Springer-Verlag, New York, NY, pp. 399–429.

Elliott, A., Brooks, N.H., 1997a. Transfer of nonsorbing solutes to a streambed with bed forms: laboratory experiments. Water Resources Research 33, 137–151.

Elliott, A., Brooks, N.H., 1997b. Transfer of nonsorbing solutes to a streambed with bed forms: theory. Water Resources Research 33, 123–136.

Erisman, J.W., van Grinsven, H., Grizzetti, B., Bouraoui, F., Powlson, D., Sutton, M.A., Bleeker, A., Reis, S., 2011. The European nitrogen problem in a global perspective. In: Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B. (Eds.), The European Nitrogen Assessment: Sources, Effects, and Policy Perspectives. Cambridge University Press, https://doi.org/10.1017/cbo9780511976988.005.

Favreau, G., Leduc, C., Marlin, C., Dray, M., Taupin, J.D., Massault, M., le Gal La Salle, C., Babic, M., 2002. Estimate of recharge of a rising water table in semiarid Niger from 3H and 14C modeling. Ground Water 40, 144–151. https://doi.org/10.1111/J.1745-6584.2002.TB02499.X.

Fetter, C.W., 2001. Applied Hydrogeology, 4th. Prentice-Hall, Upper Saddle River, NJ.

Fleckenstein, J.H., Niswonger, R.G., Fogg, G.E., 2006. River-aquifer interactions, geologic heterogeneity, and low-flow management. Ground Water 44, 837–852.

Flint, L.E., Flint, A.L., 2018. Porosity. In: Dane, J.H., Topp, C.G. (Eds.), Methods of Soil Analysis. Soil Science Society of America, Inc., Madison, WI, pp. 241–254.

Freeze, R.A., Cherry, J.A., 1979. Groundwater. Prentice Hall, Englewood Cliffs, NJ.

Gallo, F., Fossi, C., Weber, R., Santillo, D., Sousa, J., Ingram, I., Nadal, A., Romano, D., 2018. Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures. Environmental Sciences Europe 30, 13. https://doi.org/10.1186/s12302-018-0139-z.

Gardner, P.M., Heilweil, V.M., 2014. A multiple-tracer approach to understanding regional groundwater flow in the Snake Valley area of the eastern Great Basin, USA. Applied Geochemistry 45, 33–49. https://doi.org/10.1016/J.APGEOCHEM.2014.02.010.

Gavrilescu, M., Demnerová, K., Aamand, J., Agathos, S., Fava, F., 2015. Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. New Biotech 32, 147–156. https://doi.org/10.1016/J.NBT.2014.01.001.

Gelhar, L.W., Welty, C., Rehfeldt, K.R., 1992. A critical review of data on field-scale dispersion in aquifers. Water Resources Research 28, 1955–1974. https://doi.org/10.1029/92WR00607.

Gleeson, S.A., Yardley, B.W.D., Boyce, A.J., Fallick, A.E., Munz, I.A., 2000. From basin to basement: the movement of surface fluids into the crust. Journal of Geochemical Exploration 69 (70), 527–531.

Gleeson, T., Smith, L., Moosdorf, N., Hartmann, J., Dürr, H.H., Manning, A.H., van Beek, L.P.H., Jellinek, A.M., 2011. Mapping permeability over the surface of the Earth. Geophysical Research Letters 38 (2), L02401. https://doi.org/10.1029/2010gl045565.

Gonçalvès, J., Petersen, J., Deschamps, P., Hamelin, B., Baba-Sy, O., 2013. Quantifying the modern recharge of the "fossil" Sahara aquifers. Geophysical Research Letters 40, 2673–2678. https://doi.org/10.1002/GRL.50478.

Gooseff, M.N., Anderson, J.K., Wondzell, S.M., LaNier, J., Haggerty, R., 2006. A modelling study of hyporheic exchange pattern and the sequence, size, and spacing of stream bedforms in mountain stream networks, Oregon, USA. Hydrological Processes 20, 2443–2457.

Grant, G.E., Dietrich, W.E., 2017. The frontier beneath our feet. Water Resources Research 53, 2605–2609. https://doi.org/10.1002/2017WR020835.

Greene, S., Battye, N., Clark, I., Kotzer, T., Bottomley, D., 2008. Canadian Shield brine from the Con Mine, Yellowknife, NT, Canada: noble gas evidence for an evaporated Palaeozoic seawater origin mixed with glacial meltwater and Holocene recharge. Geochimica et Cosmochimica Acta 72, 4008–4019. https://doi.org/10.1016/j.gca.2008.05.058.

Guevara Ochoa, C., Medina Sierra, A., Vives, L., Zimmermann, E., Bailey, R., 2020. Spatio-temporal patterns of the interaction between groundwater and surface water in plains. Hydrological Processes 34, 1371–1392. https://doi.org/10.1002/hyp.13615.

Hallbeck, L., Pedersen, K., 2008. Characterization of microbial processes in deep aquifers of the Fennoscandian Shield. Applied Geochemistry 23, 1796–1819. https://doi.org/10.1016/j.apgeochem.2008.02.012.

Hammond, G.E., Lichtner, P.C., Lu, C., Mills, R.T., 2012. PFLOTRAN: reactive flow and transport code for use on laptops to leadership-class supercomputers. In: Zhang, F., Yeh, G.T., Parker, J.C., Shi, X. (Eds.), Ground Water Reactive Transport Models. Bentham Science Publishers, Sharjah, United Arab Emirates, pp. 141–159.

Han, D., Cao, G., McCallum, J., Song, X., 2015. Residence times of groundwater and nitrate transport in coastal aquifer systems: Daweijia area, northeastern China. Science of the Total Environment 538, 539–554. https://doi.org/10.1016/J.SCITOTENV.2015.08.036.

Hancock, P.J., Hunt, R.J., Boulton, A.J., Hancock, P.J., Boulton, A.J., Hunt, R.J., 2009. Preface: hydrogeoecology, the interdisciplinary study of groundwater dependent ecosystems. Hydrogeology Journal 17, 1–3. https://doi.org/10.1007/s10040-008-0409-8.

Hancock, P.J., Boulton, A.J., Humphreys, W.F., 2005. Aquifers and hyporheic zones: towards an ecological understanding of groundwater. Hydrogeology Journal 13, 98–111. https://doi.org/10.1007/s10040-004-0421-6.

Hao, X., Ball, B.C., Culley, J.L.B., Carter, M.R., Parkin, G.W., 2008. Soil density and porosity. In: Carter, M.R., Gregorich, E.G. (Eds.), Soil Sampling and Methods of Analysis, second ed. Taylor & Francis Group, Boca Raton, FL, pp. 743–759.

Heberer, T., 2002. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicology Letters 131, 5–17. https://doi.org/10.1016/S0378-4274(02)00041-3.

Hose, G.C., Stumpp, C., 2019. Architects of the underworld: bioturbation by groundwater invertebrates influences aquifer hydraulic properties. Aquatic Sciences 81, 20. https://doi.org/10.1007/s00027-018-0613-0.

Hose, L.D., Palmer, A.N., Palmer, M.V., Northup, D.E., Boston, P.J., DuChene, H.R., 2000. Microbiology and geochemistry in a hydrogen-sulphide-rich karst environment. Chemical Geology 169, 399–423. https://doi.org/10.1016/S0009-2541(00)00217-5.

Hotchkiss, E.R., Hall, R.O., Sponseller, R.A., Butman, D., Klaminder, J., Laudon, H., Rosvall, M., Karlsson, J., 2015. Sources of and processes controlling $CO_2$ emissions change with the size of streams and rivers. Nature Geoscience 8, 696–699. https://doi.org/10.1038/NGEO2507.

Humphreys, W.F., 2009. Hydrogeology and groundwater ecology: does each inform the other? Hydrogeology Journal 17, 5–21.

Hunter, K.S., Wang, Y., van Cappellen, P., 1998. Kinetic modeling of microbially-driven redox chemistry of subsurface environments: coupling transport, microbial metabolism and geochemistry. Journal of Hydrology 209, 53–80. https://doi.org/10.1016/S0022-1694(98)00157-7.

Jasechko, S., 2019. Global isotope hydrogeology–review. Reviews of Geophysics 57, 835–965. https://doi.org/10.1029/2018rg000627.

Jasechko, S., Birks, S.J., Gleeson, T., Wada, Y., Fawcett, P.J., Sharp, Z.D., McDonnell, J.J., Welker, J.M., 2014. The pronounced seasonality of global groundwater recharge. Water Resources Research 50, 8845–8867. https://doi.org/10.1002/2014wr015809.

Jasechko, S., Perrone, D., Befus, K.M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., Luijendijk, E., McDonnell, J.J., Taylor, R.G., Wada, Y., Kirchner, J.W., 2017. Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination. Nature Geoscience 10, 425–429. https://doi.org/10.1038/ngeo2943.

Jury, W.A., Wang, Z., 2000. Unresolved problems in vadose zone hydrology and contaminant transport. In: Faybishenko, B., Witherspoon, P.A., Benson, S.M. (Eds.), Dynamics of Fluids in Fractured Rock, Geophysical Monograph 122. American Geophysical Union, Washington, DC, pp. 67–72.

Kasahara, T., Wondzell, S.M., 2003. Geomorphic controls on hyporheic exchange flow in mountain streams. Water Resources Research 39, 1005.

Kattan, Z., 1997. Environmental isotope study of the major karst springs in Damascus limestone aquifer systems: case of the Figeh and Barada springs. Journal of Hydrology 193, 161–182. https://doi.org/10.1016/S0022-1694(96)03137-X.

Katz, B.G., Böhlke, J.K., Hornsby, H.D., 2001. Timescales for nitrate contamination of spring waters, northern Florida, USA. Chemical Geology 179, 167–186. https://doi.org/10.1016/S0009-2541(01)00321-7.

Knorr, K.H., Blodau, C., 2009. Impact of experimental drought and rewetting on redox transformations and methanogenesis in mesocosms of a northern fen soil. Soil Biology and Biochemistry 41, 1187–1198. https://doi.org/10.1016/j.soilbio.2009.02.030.

Korbel, K.L., Stephenson, S., Hose, G.C., 2019. Sediment size influences habitat selection and use by groundwater macrofauna and meiofauna. Aquatic Sciences 81, 39. https://doi.org/10.1007/s00027-019-0636-1.

Krause, S., Hannah, D.M., Fleckenstein, J.H., Heppell, C.M., Kaeser, D., Pickup, R., Pinay, G., Robertson, A.L., Wood, P.J., 2011. Inter-disciplinary perspectives on processes in the hyporheic zone. Ecohydrology 4 (4), 481–499. https://doi.org/10.1002/eco.176.

Krauss, S., Griebler, C., 2011. Pathogenic microorganisms and viruses in groundwater. Acatech Materialien Nr. 6. München, Germany.

Kreft, A., Zuber, A., 1978. On the physical meaning of the dispersion equation and its solution for different initial and boundary conditions. Chemical Engineering Science 33, 1471–1480.

Kremen, C., Williams, N.M., Thorp, R.W., 2002. Crop pollination from native bees at risk from agricultural intensification. Proceedings of the National Academy of Sciences of the United States of America 99 (26), 16812–16816. https://doi.org/10.1073pnas.262413599.

Langevin, C.D., Hughes, J.D., Banta, E.R., Niswonger, R.G., Panday, S., Provost, A.M., 2017. Documentation for the MODFLOW 6 groundwater flow model. US Geological Survey, Technical Methods, book 6, chap. A55. https://doi.org/10.3133/tm6A55.

Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environmental Pollution 163, 287–303. https://doi.org/10.1016/J.ENVPOL.2011.12.034.

Lautz, L., Siegel, D.I., 2006. Modeling surface and ground water mixing in the hyporheic zone using MODFLOW and MT3D. Advances in Water Resources 29, 1618–1633.

Le Gal La Salle, C., Aquilina, L., Fourre, E., Jean-Baptiste, P., Michelot, J.L., Roux, C., Bugai, D., Labasque, T., Simonucci, C., Van Meir, N., Noret, A., Bassot, S., Dapoigny, A., Baumier, D., Verdoux, P., Stammose, D., Lancelot, J., 2012. Groundwater residence time downgradient of Trench No. 22 at the Chernobyl Pilot Site: constraints on hydrogeological aquifer functioning. Applied Geochemistry 27, 1304–1319. https://doi.org/10.1016/j.apgeochem.2011.12.006.

Le Gal La Salle, C., Marlin, C., Leduc, C., Taupin, J.D., Massault, M., Favreau, G., 2001. Renewal rate estimation of groundwater based on radioactive tracers ($^3$H, $^{14}$C) in an unconfined aquifer in a semi-arid area, Iullemeden Basin, Niger. Journal of Hydrology 254, 145–156. https://doi.org/10.1016/S0022-1694(01)00491-7.

Long, A.J., Putnam, L.D., 2004. Linear model describing three components of flow in karst aquifers using $^{18}$O data. Journal of Hydrology 296, 254–270. https://doi.org/10.1016/J.JHYDROL.2004.03.023.

Maamar, S.B., Aquilina, L., Quaiser, A., Pauwels, H., Michon-Coudouel, S., Vergnaud-Ayraud, V., Labasque, T., Roques, C., Abbott, B.W., Dufresne, A., 2015. Groundwater isolation governs chemistry and microbial community structure along hydrologic flowpaths. Frontiers in Microbiology 6, 1457. https://doi.org/10.3389/fmicb.2015.01457.

Macpherson, G.L., 2009. $CO_2$ distribution in groundwater and the impact of groundwater extraction on the global C cycle. Chemical Geology 264, 328–336. https://doi.org/10.1016/J.CHEMGEO.2009.03.018.

Magliozzi, C., Grabowski, R.C., Packman, A.I., Krause, S., 2018. Toward a conceptual framework of hyporheic exchange across spatial scales. Hydrology and Earth System Sciences 22, 6163–6185. https://doi.org/10.5194/hess-22-6163-2018.

Maher, K., 2010. The dependence of chemical weathering rates on fluid residence time. Earth and Planetary Science Letters 294, 101–110. https://doi.org/10.1016/j.epsl.2010.03.010.

Malard, F., Tockner, K., Dole-Olivier, M.-J., Ward, J.V., 2002. A landscape perspective of surface–subsurface hydrological exchanges in river corridors. Freshwater Biology 47 (4), 621–640. https://doi.org/10.1046/j.1365-2427.2002.00906.x.

Maloszewski, P., Stichler, W., Zuber, A., 2004. Interpretation of environmental tracers in groundwater systems with stagnant water zones. Isotopes in Environmental and Health Studies 40, 21–33.

Małoszewski, P., Zuber, A., 1985. On the theory of tracer experiments in fissured rocks with a porous matrix. Journal of Hydrology 79, 333–358. https://doi.org/10.1016/0022-1694(85)90064-2.

Maloszewski, P., Zuber, A., 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers : 1. Models and their applicability. Journal of Hydrology 57, 207–231.

Marçais, J., Gauvain, A., Labasque, T., Abbott, B.W., Pinay, G., Aquilina, L., Chabaux, F., Viville, D., de Dreuzy, J.R., 2018. Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers. Science of the Total Environment 636, 260–272. https://doi.org/10.1016/j.scitotenv.2018.04.196.

Marzadri, A., Tonina, D., Bellin, A., Valli, A., 2016. Mixing interfaces, fluxes, residence times and redox conditions of the hyporheic zones induced by dune-like bedforms and ambient groundwater flow. Advances in Water Resources 88, 139–151. https://doi.org/10.1016/j.advwatres.2015.12.014.

Matthess, G., Pekdeger, A., 1981. Concepts of a survival and transport model of pathogenic bacteria and viruses in groundwater. The Science of the Total Environment 21, 149–159. https://doi.org/10.1016/0048-9697(81)90148-0.

McCallum, J.L., Cook, P.G., Simmons, C.T., 2015. Limitations of the use of environmental tracers to infer groundwater age. Groundwater 53, 56–70. https://doi.org/10.1111/gwat.12237.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnston, C.A., Mayorga, E., McDowell, W.H., Pinay, G., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6, 301–312. https://doi.org/10.1007/s10021-003-0161-9.

Meckenstock, R.U., Elsner, M., Griebler, C., Lueders, T., Stumpp, C., Aamand, J., Agathos, S.N., Albrechtsen, H.J., Bastiaens, L., Bjerg, P.L., Boon, N., Dejonghe, W., Huang, W.E., Schmidt, S.I., Smolders, E., Sørensen, S.R., Springael, D., Van Breukelen, B.M., 2015. Biodegradation: updating the concepts of control for microbial cleanup in contaminated aquifers. Environmental Science and Technology 49, 7073–7081. https://doi.org/10.1021/acs.est.5b00715.

Meyer, J.L., Strayer, D.L., Wallace, J.B., Eggert, S.L., Helfman, G.S., Leonard, N.E., 2007. The contribution of headwater streams to biodiversity in river networks. Journal of the American Water Resources Association 43 (1), 86–103. https://doi.org/10.1111/j.1752-1688.2007.00008.x.

Mitchell, C.P.J., Branfireun, B.A., 2005. Hydrogeomorphic controls on reduction-oxidation conditions across boreal upland-peatland interfaces. Ecosystems 8, 731–747. https://doi.org/10.1007/s10021-005-1792-9.

Moeck, C., Grech-Cumbo, N., Podgorski, J., Bretzler, A., Gurdak, J.J., Berg, M., Schirmer, M., 2020. A global-scale dataset of direct natural groundwater recharge rates: a review of variables, processes and relationships. Science of the Total Environment 717, 137042. https://doi.org/10.1016/j.scitotenv.2020.137042.

Mohrig, D., Smith, J.D., 1996. Predicting the migration rates of subaqueous dunes. Water Resources Research 32, 3207–3217. https://doi.org/10.1029/96WR01129.

Monroe, W.H., 1970. A glossary of karst terminology. US Geological Survey, Water-Supply Paper 1899-K, Washington, DC.

Montgomery, D.R., Buffington, J.M., 1997. Channel-reach morphology in mountain drainage basins. Geological Society of America Bulletin 109 (5), 596–611.

Neuman, S.P., 2005. Trends, prospects and challenges in quantifying flow and transport through fractured rocks. Hydrogeology Journal 13, 124–147. https://doi.org/10.1007/s10040-004-0397-2.

Newman, B.D., Wilcox, B.P., Archer, S.R., Breshears, D.D., Dahm, C.N., Duffy, C.D., McDowell, N.G., Phillips, F.M., Scanlon, B.R., Vivoni, E.R., 2006. Ecohydrology of water-limited environments: a scientific vision. Water Resources Research 42, W06302.

Nikolaou, A., Meric, S., Fatta, D., 2007. Occurrence patterns of pharmaceuticals in water and wastewater environments. Analytical and Bioanalytical Chemistry 387, 1225–1234. https://doi.org/10.1007/S00216-006-1035-8.

Nunes, F.L.D., Aquilina, L., De Ridder, J., Francez, A.J., Quaiser, A., Caudal, J.P., Vandenkoornhuyse, P., Dufresne, A., 2015. Time-scales of hydrological forcing on the geochemistry and bacterial community structure of temperate peat soils. Scientific Reports 5 (14612). https://doi.org/10.1038/srep14612.

Otto, I.M., Donges, J.F., Cremades, R., Bhowmik, A., Hewitt, R.J., Lucht, W., Rockström, J., Allerberger, F., McCaffrey, M., Doe, S.S.P., Lenferna, A., Morán, N., van Vuuren, D.P., Schellnhuber, H.J., 2020. Social tipping dynamics for stabilizing Earth's climate by 2050. Proceedings of the National Academy of Sciences of the United States of America 117, 2354–2365. https://doi.org/10.1073/pnas.1900577117.

Packman, A.I., Salehin, M., Zaramella, M., 2004. Hyporheic exchange with gravel beds: basic hydrodynamic interactions and bedform-induced advective flows. Journal of Hydraulic Engineering 130 (7), 647–656.

Palcsu, L., Gessert, A., Túri, M., Kovács, A., Futó, I., Orsovszki, J., Puskás-Preszner, A., Temovski, M., Koltai, G., 2021. Long-term time series of environmental tracers reveal recharge and discharge conditions in shallow karst aquifers in Hungary and Slovakia. Journal of Hydrology: Regional Studies 36, 100858. https://doi.org/10.1016/J.EJRH.2021.100858.

Pandey, P.K., Kass, P.H., Soupir, M.L., Biswas, S., Singh, V.P., 2014. Contamination of water resources by pathogenic bacteria. AMB Express 4, 1–16. https://doi.org/10.1186/S13568-014-0051-X.

Pedersen, K., 1997. Microbial life in deep granitic rock. FEMS Microbiology Reviews 20, 399–414. https://doi.org/10.1016/S0168-6445(97)00022-3.

Peterson, B.J., Wollheim, W.M., Mulholland, P.J., Webster, J.R., Meyer, J.L., Tank, J.L., Marti, E., Bowden, W.B., Valett, H.M., Hershey, A.E., McDowell, W.H., Dodds, W.K., Hamilton, S.K., Gregory, S., Morrall, D.D., 2001. Control of nitrogen export from watersheds by headwater streams. Science 292, 86–90. https://doi.org/10.1126/science.1056874.

Pledger, A.G., Rice, S.P., Millett, J., 2017. Foraging fish as zoogeomorphic agents: an assessment of fish impacts at patch, barform, and reach scales. Journal of Geophysical Research: Earth Surface 122, 2105–2123. https://doi.org/10.1002/2017JF004362.

Racchetti, E., Bartoli, M., Soana, E., Longhi, D., Christian, R.R., Pinardi, M., Viaroli, P., 2011. Influence of hydrological connectivity of riverine wetlands on nitrogen removal via denitrification. Biogeochemistry 103, 335–354. https://doi.org/10.1007/s10533-010-9477-7.

Renard, P., Allard, D., 2013. Connectivity metrics for subsurface flow and transport. Advances in Water Resources 51, 168–196. https://doi.org/10.1016/j.advwatres.2011.12.001.

Rezanezhad, F., Price, J.S., Quinton, W.L., Lennartz, B., Milojevic, T., van Cappellen, P., 2016. Structure of peat soils and implications for water storage, flow and solute transport: a review update for geochemists. Chemical Geology 429, 75–84. https://doi.org/10.1016/J.CHEMGEO.2016.03.010.

Rhoades, C.C., Fegel, T.S., Covino, T.P., Dwire, K.A., Elder, K., 2021. Sources of variability in springwater chemistry in Fool Creek, a high-elevation catchment of the Rocky Mountains, Colorado, USA. Hydrological Processes 35, e14089. https://doi.org/10.1002/hyp.14089.

Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. Water Research 42, 4215–4232. https://doi.org/10.1016/J.WATRES.2008.07.020.

Roche, K.R., Li, A., Bolster, D., Wagner, G.J., Packman, A.I., 2019. Effects of turbulent hyporheic mixing on reach-scale transport. Water Resources Research 55, 3780–3795. https://doi.org/10.1029/2018WR023421.

Röling, W.F.M., Van Breukelen, B.M., Braster, M., Lin, B., Van Verseveld, H.W., 2001. Relationships between microbial community structure and hydrochemistry in a landfill leachate-polluted aquifer. Applied and Environmental Microbiology 67, 4619–4629. https://doi.org/10.1128/AEM.67.10.4619-4629.2001.

Roques, C., 2013. Hydrogéologie des zones de faille du socle cristallin: implications en terme de ressources en eau pour le Massif Armoricain. PhD thesis. Université Rennes 1. URL. http://www.theses.fr/2013REN1S138 (accessed 10.06.2022).

Rosenberry, D.O., Glaser, P.H., Siegel, D.I., 2006. The hydrology of northern peatlands as affected by biogenic gas: current developments and research needs. Hydrological Processes 20, 3601–3610. https://doi.org/10.1002/hyp.6377.

Sansom, B.J., Atkinson, J.F., Bennett, S.J., 2018. Modulation of near-bed hydrodynamics by freshwater mussels in an experimental channel. Hydrobiologia 810, 449–463. https://doi.org/10.1007/s10750-017-3172-9.

Screaton, E., Martin, J.B., Ginn, B., Smith, L., 2004. Conduit properties and karstification in the unconfined Floridan Aquifer. Ground Water 42, 338–346. https://doi.org/10.1111/J.1745-6584.2004.TB02682.X.

Soulsby, C., Tetzlaff, D., van den Bedem, N., Malcolm, I.A., Bacon, P.J., Youngson, A.F., 2007. Inferring groundwater influences on surface water in montane catchments from hydrochemical surveys of springs and streamwaters. Journal of Hydrology 333, 199–213. https://doi.org/10.1016/j.jhydrol.2006.08.016.

Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S.T., Benettin, P., Dubbert, M., Hartmann, A., Hrachowitz, M., Kirchner, J.W., McDonnell, J.J., Orlowski, N., Penna, D., Pfahl, S., Rinderer, M., Rodriguez, N., Schmidt, M., Werner, C., 2019. The demographics of water: a review of water ages in the critical zone. Reviews of Geophysics 57, 800–834. https://doi.org/10.1029/2018rg000633.

Stanford, J.A., Ward, J.V., 1993. An ecosystem perspective of alluvial rivers: connectivity and the hyporheic corridor. Journal of the North American Benthological Society 12, 48–60.

Statzner, B., Arens, M.-F., Champagne, J.-Y., Morel, R., Herouin, R., 1999. Silk-producing steam insects and gravel erosion: significant biological effects on critical shear stress. Water Resources Research 35 (11), 3495–3506.

Steffen, W., Richardson, K., Rockström, J., Cornell, S.E., Fetzer, I., Bennett, E.M., Biggs, R., Carpenter, S.R., De Vries, W., De Wit, C.A., Folke, C., Gerten, D., Heinke, J., Mace, G.M., Persson, L.M., Ramanathan, V., Reyers, B., Sörlin, S., 2015. Planetary boundaries: guiding human development on a changing planet. Science 347 (6223). https://doi.org/10.1126/science.1259855.

Stein, H., Griebler, C., Berkhoff, S., Matzke, D., Fuchs, A., Hahn, H.J., 2012. Stygoregions - a promising approach to a bioregional classification of groundwater systems. Scientific Reports 2, 673. https://doi.org/10.1038/srep00673.

Storey, R.G., Howard, K.W.F., Williams, D.D., 2003. Factors controlling riffle-scale hyporheic exchange flows and their seasonal changes in gaining stream: a three-dimensional groundwater model. Water Resources Research 39, 17. https://doi.org/10.1029/2002WR001367.

Stuart, M.E., Maurice, L., Heaton, T.H.E., Sapiano, M., Micallef Sultana, M., Gooddy, D.C., Chilton, P.J., 2010. Groundwater residence time and movement in the Maltese islands – a geochemical approach. Applied Geochemistry 25, 609–620. https://doi.org/10.1016/j.apgeochem.2009.12.010.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd. Wiley, New York, NY.

Stumpp, C., Hose, G.C., 2017. Groundwater amphipods alter aquifer sediment structure. Hydrological Processes 31, 3452–3454. https://doi.org/10.1002/hyp.11252.

Stumpp, C., Żurek, A.J., Wachniew, P., Gargini, A., Gemitzi, A., Filippini, M., Witczak, S., 2016. A decision tree tool supporting the assessment of groundwater vulnerability. Environmental Earth Sciences 75, 1057. https://doi.org/10.1007/s12665-016-5859-z.

Suckow, A., 2014. The age of groundwater – definitions, models and why we do not need this term. Applied Geochemistry 50, 222–230. https://doi.org/10.1016/j.apgeochem.2014.04.016.

Taylor, C.J., Greene, E.A., 2008. Hydrogeologic characterization and methods used in the investigation of karst hydrology. In: Rosenberry, D.O., LaBaugh, J.W. (Eds.), Field Techniques for Estimating Water Fluxes Between Surface Water and Ground Water. US Geological Survey, Techniques and Methods 4-D2, pp. 75–114.

Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Philosophical Transactions of the Royal Society B: Biological Sciences 364, 2027–2045. https://doi.org/10.1098/RSTB.2008.0284.

Therrien, R., McLaren, R.G., Sudicky, E.A., Panday, S.M., 2010. HydroGeoSphere: a three-dimensional numerical model describing fully-integrated subsurface and surface flow and solute transport. Groundwater Simulations Group, URL https://www.ggl.ulaval.ca/fileadmin/ggl/documents/rtherrien/hydrogeosphere.pdf.

Thulin, B., Hahn, H.J., 2008. Ecology and living conditions of groundwater fauna. Technical Report TR-08-06. Swedish Nuclear Fuel and Waste Management CO, Stockholm.

Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., Schindler, D., Schlesinger, W.H., Simberloff, D., Swackhamer, D., 2001. Forecasting agriculturally driven global environmental change. Science 292, 281–284. https://doi.org/10.1126/science.1057544.

Tonina, D., Bellin, A., 2008. Effects of pore-scale dispersion, degree of heterogeneity, sampling size, and source volume on the concentration moments of conservative solutes in heterogeneous formations. Advances in Water Resources 31, 339–354. https://doi.org/10.1016/j.advwatres.2007.08.009.

Tonina, D., Buffington, J.M., 2007. Hyporheic exchange in gravel-bed rivers with pool-riffle morphology: laboratory experiments and three-dimensional modeling. Water Resources Research 43, W01421. https://doi.org/10.1029/2005WR004328.

Tonina, D., Buffington, J.M., 2009a. A three-dimensional model for analyzing the effects of salmon redds on hyporheic exchange and egg-pocket habitat. Canadian Journal of Fisheries and Aquatic Science 66, 2153–2157. https://doi.org/10.1139/F09-146.

Tonina, D., Buffington, J.M., 2009b. Hyporheic exchange in mountain rivers I: Mechanics and environmental effects. Geography Compass 3 (3), 1063–1086. https://doi.org/10.1111/j.1749-8198.2009.00226.x.

Tonina, D., de Barros, F.P.J., Marzadri, A., Bellin, A., 2016. Does streambed heterogeneity matter for hyporheic residence time distribution in sand-bedded streams? Advances in Water Resources 96, 120–126. https://doi.org/10.1016/j.advwatres.2016.07.009.

Tóth, J., 1963. A theoretical analysis of groundwater flow in small drainage basins. Journal of Geophysical Research 68, 4795–4812.

Tufenkji, N., 2007. Modeling microbial transport in porous media: traditional approaches and recent developments. Advances in Water Resources 30, 1455–1469.

Turnadge, C., Smerdon, B.D., 2014. A review of methods for modelling environmental tracers in groundwater: advantages of tracer concentration simulation. Journal of Hydrology 519, 3674–3689. https://doi.org/10.1016/j.jhydrol.2014.10.056.

van der Velde, Y., de Rooij, G.H., Rozemeijer, J.C., van Geer, F.C., Broers, H.P., 2010. Nitrate response of a lowland catchment: on the relation between stream concentration and travel time distribution dynamics. Water Resources Research 46, W11534. https://doi.org/10.1029/2010WR009105.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications 7, 737–750. https://doi.org/10.2307/2269431.

Waber, H.N.N., Smellie, J.a.T.A.T., 2008. Characterisation of pore water in crystalline rocks. Applied Geochemistry 23, 1834–1861. https://doi.org/10.1016/j.apgeochem.2008.02.007.

Wachniew, P., Zurek, A., Stumpp, C., Gemitzi, A., Gargini, A., Filippini, M., Rozanski, K., Meeks, J., Kvaerner, J., Witczak, S., 2016. Toward operational methods for the assessment of intrinsic groundwater vulnerability: a review. Critical Reviews in Environmental Science and Technology 46, 827–884. https://doi.org/10.1080/10643389.2016.1160816.

Ward, N.D., Bianchi, T.S., Medeiros, P.M., Seidel, M., Richey, J.E., Keil, R.G., Sawakuchi, H.O., 2017. Where carbon goes when water flows: carbon cycling across the aquatic continuum. Frontiers in Marine Science 4, 7. https://doi.org/10.3389/FMARS.2017.00007/PDF.

White, A.F., Bullen, T.D., Vivit, D.V., Schultz, M.S., Clow, D.W., 1999. The role of disseminated calcite in the chemical weathering of granitoid rocks. Geochimica et Cosmochimica Acta 63 (13/14), 1939−1953.

White, W.B., 2002. Karst hydrology: recent developments and open questions. Engineering Geology 65, 85−105. https://doi.org/10.1016/S0013-7952(01)00116-8.

Williams, M.D., Oostrom, M., 2000. Oxygenation of anoxic water in a fluctuating water table system: an experimental and numerical study. Journal of Hydrology 230, 70−85. https://doi.org/10.1016/S0022-1694(00)00172-4.

Williams, P.W., 2008. The role of the epikarst in karst and cave hydrogeology: a review. International Journal of Speleology 37 (1), 1−10. https://doi.org/10.5038/1827-806X.37.1.1.

Winter, T.C., Harvey, J.W., Franke, O.L., Alley, W.M., 1998. Ground water and surface water: a single resource. US Geological Survey, Circular 1139, Denver, CO.

Wondzell, S.M., Swanson, F.J., 1996. Seasonal and storm dynamics of the hyporheic zone of a 4$^{th}$ order mountain stream. 1: Hydrologic processes. Journal of the North American Benthological Society 15, 3−19.

Wondzell, S.M., Swanson, F.J., 1999. Floods, channel change, and the hyporheic zone. Water Resources Research 35, 555−567.

Wörman, A., Packman, A.I., Marklund, L., Harvey, J.W., 2006. Exact three-dimensional spectral solution to surface-groundwater interaction with arbitrary surface topography. Geophysical Research Letters 33, L07402.

Worthington, S.R.H., Davies, G.J., Alexander, E.C., 2016. Enhancement of bedrock permeability by weathering. Earth-Science Reviews 160, 188−202. https://doi.org/10.1016/j.earscirev.2016.07.002.

Wroblicky, G.J., Campana, M.E., Valett, H.M., Dahm, C.N., 1998. Seasonal variation in surface-subsurface water exchange and lateral hyporheic area of two stream-aquifer systems. Water Resources Research 34, 317−328.

Zarnetske, J.P., Haggerty, R., Wondzell, S.M., Baker, M.A., 2011. Dynamics of nitrate production and removal as a function of residence time in the hyporheic zone. Journal of Geophysical Research: Biogeosciences 116, G01025.

Ziebis, W., Forster, S., Huettel, M., Jørgensen, B.B., 1996. Complex burrows of mud shrimp *Callianassa truncata* and their geochemical impact in the sea bed. Nature 382 (6592), 619−622.