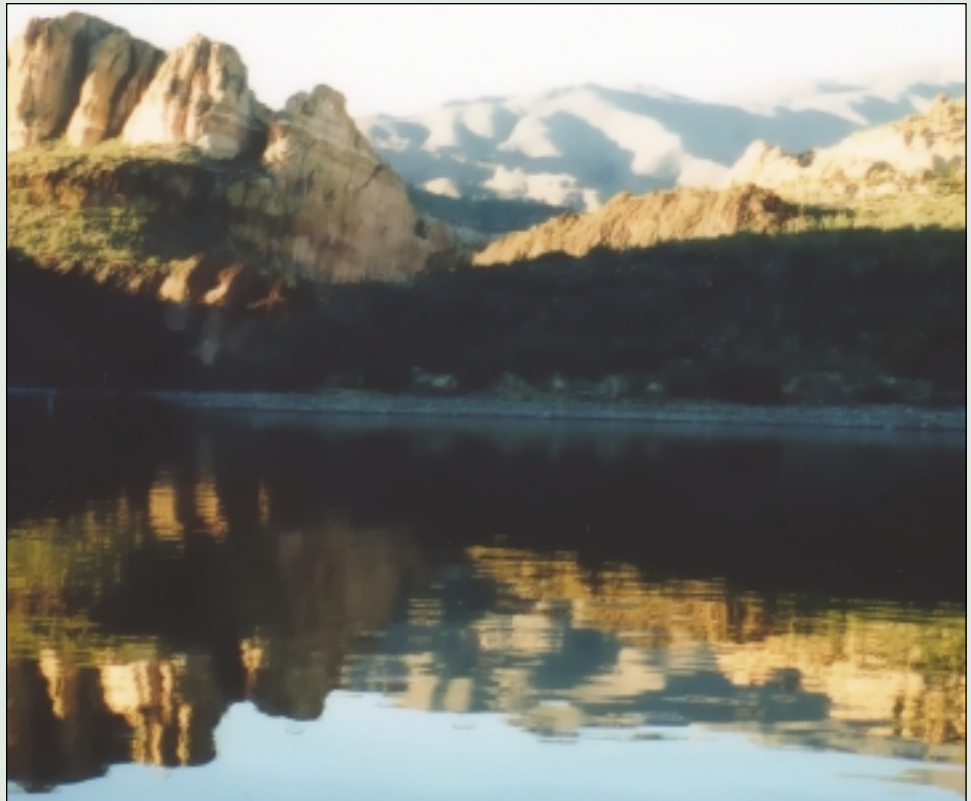


CHAPTER 3

PHYSICAL-CHEMICAL CHARACTERISTICS OF WATER

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Apache Reservoir, Arizona. *Photo courtesy D. Walker.*

3.1 THE WATERY PLANET

3.1.1 Distribution

Ninety seven per cent of water on the Earth is marine (salt-water), while only 3% is freshwater (Figure 3.1). With regard to the freshwater, 79% is stored in polar ice caps and mountain glaciers, 20% is stored in aquifers or soil moisture, and 1% is surface water (primarily lakes and rivers). An estimated 110,000 km³ of rain, snow, and ice falls annually on land surfaces, and this is what replenishes fresh water resources. Possible effects of global warming, combined with continued increases in human population and economic development are resulting in critical concern for the future sustainability of freshwater resources.

The limited supplies of surface waters and groundwater receive significant amounts of the pollutants generated by humans. Lakes across the planet have an average retention time of 100 years, meaning it takes 100 years to replace that volume of water. Rivers, on the other hand, have a much shorter retention time. The relatively long retention time in lakes highlights the danger of introducing pollutants that will be present for a long time (*i.e.*, they are “environmentally persistent”). The short retention time in rivers means that pollutants are transferred rapidly to other areas such as groundwater or oceans. The retention time of groundwater is measured in hundreds if not thousands of years. In the groundwater environment, persistent pollutants may remain intact for extremely long periods because of constraints to transformation. The characteristics of groundwater are described in Section 3.10. Pollution of groundwater and surface water is discussed in Chapters 17 and 18, respectively.

Pollutants in the ocean may be introduced into the food chain by filter-feeding organisms or possibly may be sequestered in cold, deep basins where they are resistant to degradation by natural processes. Much of the world’s population inhabits coastal areas, making oceans especially

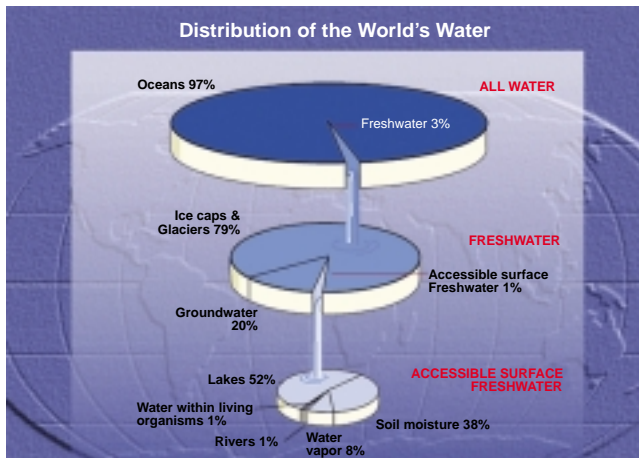


Figure 3.1 Distribution of the world’s water (http://earth.rice.edu/mtpe/hydro/hydrosphere/hot/freshwater/0water_chart.html)

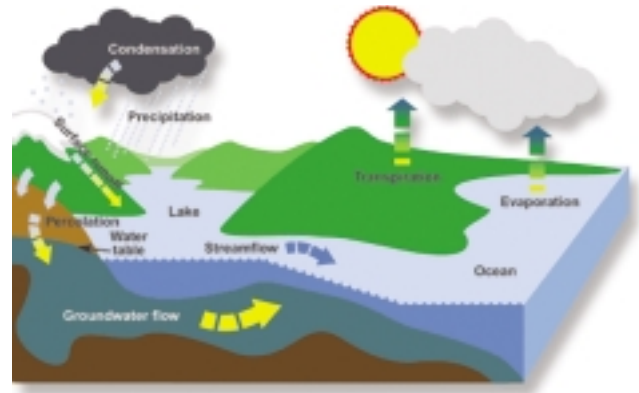


Figure 3.2 The hydrologic cycle. (http://www.ec.gc.ca/water/en/nature/prop/e_cycle.htm)

vulnerable to pollutants introduced directly or from surface water and groundwater drainage.

3.1.2 The Hydrologic Cycle

Water covers much more of earth’s surface than does land. The continual movement of water across the earth due to evaporation, condensation, or precipitation is called the hydrologic cycle (Figure 3.2). The consistency of this cycle has taken millennia to establish, but can be greatly altered by human activities including global warming, desertification, or excessive groundwater pumping. Water, in its constantly changing and various forms, has been and continues to be an important factor driving evolutionary processes in all living things.

Evaporating water moderates temperature; clouds and water vapor protect us from various forms of radiation; and precipitation spreads water to all regions of the globe, allowing life to flourish from the highest peaks to the deepest caves. Solar energy drives evaporation from open water surfaces as well as soil and plants. Air currents distribute this vaporized water around the globe. Cloud formation, condensation, and precipitation are functions of cooling. When vaporized, water cools to a certain temperature, condensation occurs, and often results in precipitation to the earth’s surface. Once back on the surface of the earth, whether on land or water, solar energy then continues the cycle. The latent heat of water (the energy that is required or released as water changes states) serves to moderate global temperatures, maintaining them in a range suitable for humans and other living organisms.

Some processes involved with the hydrologic cycle aid in purifying water of the various contaminants accumulated during its cycling. For instance, precipitation reaching the soil will allow weak acids absorbed from air to react with various minerals and neutralize the acids. Suspended sediments entrained through erosion and runoff will settle out as the water loses velocity in ponds or lakes. Other solids will be filtered out as water percolates through soil and vadose zones and ultimately to an aquifer. Many organic compounds will be degraded by bacteria in soil or sediments.

Salts and other dissolved solids will be left behind as water evaporates and returns to a gaseous phase or freezes into a solid phase (ice). These processes maintained water quality of varying degrees before human impacts on the environment; however, the current scale of these impacts often tends to overwhelm the ability of natural systems to cleanse water through the hydrologic cycle. Further, we have introduced many compounds that are resistant to normal removal or degradation processes (Chapters 16–18).

3.2 UNIQUE PROPERTIES OF WATER

3.2.1 Structure and Polarity

Water is an unusual molecule in that the structure of two hydrogen atoms and one oxygen atom provides several characteristics that make it a universal solvent. First is the fact that the two hydrogen atoms, situated on one side of the oxygen atom, carry positive charges, while the oxygen atom retains a negative charge (Figure 3.3).

This induced polarity allows water molecules to attract both positive and negative ions to the respective poles of the molecule. It also causes water molecules to attract one another. This contributes to the viscosity of water and to the alignment that water molecules will take when temperatures decrease to the point of ice formation. The fact that water becomes less dense in its solid state, compared to its liquid state, is yet another unusual characteristic. Because of this, ice floats and insulates deeper water. This is critical to maintaining deep bodies of liquid waters on Earth rather than a thin layer of water on top of an increasingly deep bed of solid ice.

The bipolar nature of water and its attraction to other polar compounds makes it an easy conduit for the dissolution and transport for any number of pollutants. Because so many materials dissolve so completely in water, their removal from water is often difficult.

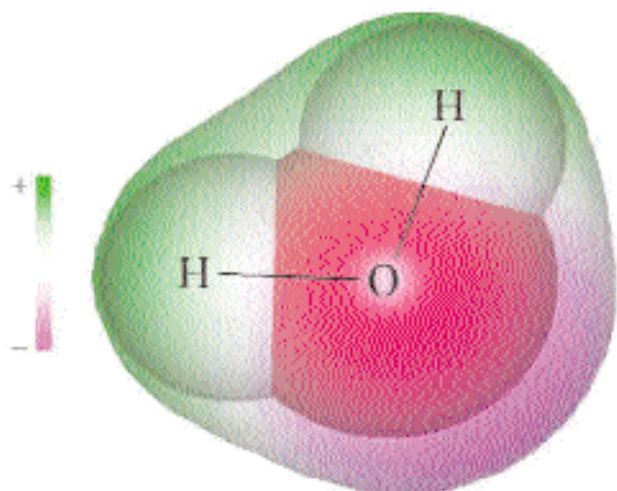


Figure 3.3 Structure and charge distribution of water. (<http://faculty.uca.edu/~benw/biol/400/notes32.htm>)

3.2.2 Thermal Properties

Water has unique thermal properties that enable it to exist in three different states: vapor; solid; and liquid under environmentally relevant conditions. Changes in each phase have certain terminology, depending upon state changes, as described below:

Condensation: vapor → liquid

Evaporation: liquid → vapor

Freezing: liquid → solid

Melting: solid → liquid

Sublimation: solid → vapor

Frost Formation: vapor → solid

Most liquids contract with decreasing temperature. This contraction also makes these liquids denser (*i.e.*, “heavier”) as temperature decreases. Water is unique because its density increases only down to approximately 4°C, at which point it starts to become less dense (Figure 3.4). This is important because without this unique property, icebergs and other solid forms of water would sink to the bottom of the ocean, displacing liquid water as they did so. Also, lakes and ponds would freeze from the bottom up with the same effect.

The **specific heat** of water is the amount of energy required to raise one gram of water, one degree C, and is usually expressed as *joules per gram-degree Celsius* ($\text{J g}^{-1}\text{°C}^{-1}$). Specific heat values for the different phases of water are given below.

PHASE	$\text{J g}^{-1}\text{°C}^{-1}$
Vapor	2.02
Liquid	4.18
Solid	2.06

The **latent heat of fusion** is the amount of energy required to change 1 gram of ice, at its melting point temperature, to liquid. It is considered “latent” because there is no temperature change associated with this energy transfer, only a change in phase. The heat of fusion for water is $-333 \text{ J g}^{-1}\text{°C}^{-1}$.

The energy required for the phase changes of water are given in Table 3.1.

Earth is unique because it contains the necessary temperatures and pressures for all three states of water to exist. Water, under the correct combination of temperature and pressure, is capable of existing in all three states (solid, liquid, and vapor) simultaneously and in equilibrium. This is referred to as the *triple point*, where infinitesimally small increases or decreases in either pressure or temperature will cause water to be either a liquid, solid, or gas. Specifically, the triple point of water exists at a temperature and pressure of 273.16 Kelvin (0.0098°C) and 611.73 pascals (0.00603 atm) respectively. Figure 3.5 shows that decreasing temperature and increasing pressure causes water to pass directly from a

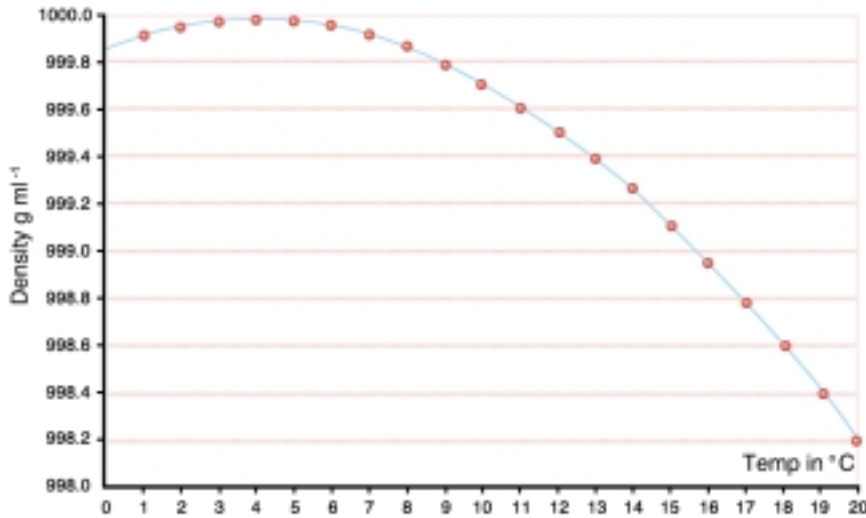


Figure 3.4 The density of water at varying temperatures. (<http://www.cyberlaboratory.com/library/basicsofdensity/whatisdensity.htm>)

gas to a solid. At pressures higher than the triple point, increasing temperature causes solid water (ice) to transform into liquid and eventually gas (vapor). Liquid water cannot exist in pressures lower than the triple point and ice instantaneously becomes steam with increasing temperature. This process is known as sublimation.

3.3 MECHANICAL PROPERTIES

3.3.1 Interception, Evaporation, Infiltration, Runoff

Precipitation in a nonpolluted environment provides a fairly pure form of water. However, today precipitation may absorb pollutant gases in the environment to form acid rain (see also Chapter 23). Precipitation can also pick up fine particulates that were suspended in the air. As the forms of precipitation reach the surface, they are likely to fall upon and be intercepted by various types of vegetation. In many regions, much of the precipitation may settle in or on trees, shrubs, or grasses and never actually reach the ground. In others, the plants may slow the rate of fall of raindrops, break them into smaller drops, or channel them more gently to the surface. Interception leads to several factors that impact the water and its role with later pollution events. First, the water

may evaporate directly from the plant, never reaching the soil. Second, it may entrain materials settled on the plant surfaces. Third, by slowing the momentum and reducing the energy of falling rain, physical impacts on the soil and resulting erosion may be reduced.

Certain anthropogenic land use practices or natural events can lead to decreases in interception and subsequent increases in sediment suspended within water. Often, sediment may have other pollutants attached to it thereby polluting the water as well. Certain mining practices, if not re-vegetated, can result in increased erosion resulting in contamination of streams. Natural events, such as wildfires, can also result in substantial erosion and contamination of downstream areas (see also Chapter 16).

Evaporation of water is another crucial part of the hydrologic cycle. The rate of evaporation from a body of

TABLE 3.1 Phase changes of water.

PROCESS	FROM	TO	ENERGY GAINED OR LOST (J g ⁻¹ °C ⁻¹)
Condensation	Vapor	Liquid	2500
Deposition	Vapor	Ice	2833
Evaporation	Liquid	Vapor	-2500
Freezing	Liquid	Ice	333
Melting	Ice	Liquid	-333
Sublimation	Ice	Vapor	2833

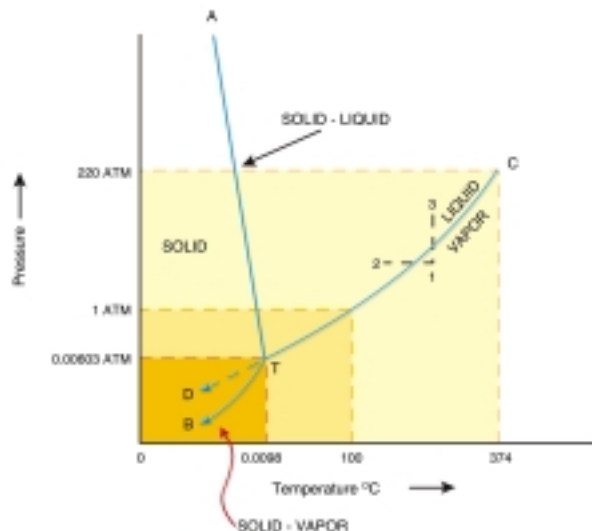


Figure 3.5 Phase diagram of the triple point of water. (http://www.sv.vt.edu/classes/MSE2094_NoteBook/96ClassProj/pics/trip_pt1)



Figure 3.6 This satellite image is of the Great Salt Lake in Utah. This is the largest lake in the U.S. west of the Mississippi River covering some 1,700 square miles. It is also 3 to 5 times more saline than the world's oceans. It is a fishless lake with only the most saline-tolerant (“halophytic”) organisms capable of surviving. The largest organisms inhabiting its waters are species of brine shrimp and brine flies. (<http://ut.water.usgs.gov/greatsaltlake/>)

water, or mass of soil, is a function of the relative humidity, temperature, and wind speed. An important subcomponent of evaporation is transpiration, the active transport and evaporation of water from plants. Plants transport nutrients in an aqueous solution and then dispose of the water through their leaves by evaporation. As water evaporates, it leaves a concentrated amount of compounds that were formerly dissolved in that water. This applies to nutrients left in plants, as well as to pollutants that were introduced with the water.

Water that is not contained in oceans is often referred to as “freshwater,” implying that it is not saline. This is not always the case, and some inland waters can be much more saline than the world's oceans. This is especially true in arid environments or enclosed basins that have limited or no drainage. Often, salinity in inland waters reaches such high levels that it supports little, if any, life. Salinity in inland waters, and in the world's oceans, is largely a result of evaporation. As water is vaporized and once again enters the hydrologic cycle, salts accumulate on the earth's surface, and in lieu of adequate dilution and flushing, can often make water increasingly saline (Figure 3.6).

Precipitation that reaches the soil surface either infiltrates the ground or runs off the surface. Human uses of water also deliver enormous amounts of water onto soils or human-made structures that can either infiltrate or contribute to run-off.

This is a major source of pollutants introduced into the environment. The infiltration rate of water into the ground is an important measure used to determine how foundations and sewer systems are designed, how irrigation water should be applied, and how pollutants may migrate to a water supply.

How water runs off of surfaces is also a matter of interest to hydrology, fisheries, aquatic biology, and pollution science. Not only are pollutants entrained in flowing water, but erosion and flooding can also occur. Studies of run off and surface flow focus upon the amounts of soil and pollutants that are transported and their eventual fate as they arrive into lakes or streams.

3.4 THE UNIVERSAL SOLVENT

One of the most unique properties of water is its ability to dissolve other substances. It is this ability that can lead to large-scale landscape transformations (Figure 3.7), and the



Figure 3.7 The Grand Canyon of the Colorado River was formed by the dissolution and erosion of material over eons. Historically, most of this material was deposited in the Gulf of California. With the construction of large dams along the course of the Colorado River, most of this material is now deposited in storage reservoirs. (<http://www.kaibab.org/tr961/lg961110.jpg>)

TABLE 3.2 Examples of typical concentrations of solutes in water.

Percent		parts per hundred	10^2
Milligram	mg L^{-1}	parts per million	10^6
Microgram	$\mu\text{g L}^{-1}$	parts per billion	10^9
Nanogram	ng L^{-1}	parts per trillion	10^{12}

ability to carry contaminants relatively long distances. If it were not for the various substances dissolved in water, an organism's cells would quickly be deprived of essential nutrients, salts, and gasses, leading to eventual death. The dissolution of materials in water has shaped the nature of all living creatures on the planet.

3.4.1 Concentration Terminology

It is important to quantify the amount of material dissolved in water. Quantification require a range of values so that we can determine high versus low concentrations for a given constituent. The values are always expressed as a ratio of solute to water (Table 3.2). The importance of very small concentrations should never be underestimated. This is especially true in toxicological studies where very small concentrations can lead to toxic impacts on organisms (Chapter 13).

There are two major expressions in concentration terminology.

- Mass/mass. An example would be parts per million (ppm), which equals parts of solution/parts of material $\times 10^6$.
- Mass/volume. An example would be milligrams/liter (mg L^{-1}), which equals milligrams of dissolved solid(s)/liter of solution.

Most of the time, mg L^{-1} and ppm will be the same number. Their relationship is that the specific gravity of solution \times ppm = mg L^{-1} . Note that this same relationship holds true when using other concentrations such as parts per billion (ppb) and $\mu\text{g L}^{-1}$ or parts per trillion and ng L^{-1} .

EXAMPLE CALCULATION 3.1

Using Concentration

Knowing the concentrations of constituents in water has many utilitarian uses. For example, a farmer may want to know how much salt will accumulate in the soil on his property when using water where both sodium (Na) and chloride (Cl) concentrations are known.

- Suppose the water contained 35 ppm Cl and 23 pm Na (*i.e.*, 58 ppm NaCl).
- How many pounds of Na, Cl, and NaCl are contained in an acre foot of water? (1 acre foot = 1 acre of land with a water depth of 1 foot).

To calculate this we assume the following:

- Water weighs 8.33 pounds^{-1} gallon.
- There are $7.5 \text{ gallons ft}^{-3}$ and this therefore weighs 62.43 pounds.
- One acre foot = $43,560 \text{ ft}^3$
- So, $43,560 \text{ ft}^3 \times 62.42 \text{ pounds ft}^{-3} = 2,718,144$ pounds of solution.
- Therefore, $2,718,144 \times 0.000023$ (or 23 ppm) = 62.5 pounds of Na and $2,718,144 \times 0.000035$ (or 35 ppm) = 95.1 pounds of Cl.
- $62.5 \text{ (Na)} + 95.1 \text{ (Cl)} = 157.7$ pounds of NaCl.

Now that the farmer knows how much is in one acre foot, if the rate of water flow onto his crops is known, he can calculate an accumulation rate. For instance, let's say the farmer wants to know how many tons day^{-1} and tons year^{-1} of NaCl flow onto his crops and into his soil if the flow is held constant at $2 \text{ ft}^3 \text{ second}^{-1}$ (commonly written as cfs for "cubic feet per second").

- $2.0 \text{ cfs } 3600 \text{ sec hour}^{-1} \times 24 \text{ hr day}^{-1} \times 62.4 \text{ pounds ft}^{-3} \times 0.000058$ (58 ppm) = 625 pounds NaCl day^{-1} .
- $2000 \text{ pounds ton}^{-1}$ divided by 625 pounds = 0.313 tons NaCl day^{-1} .
- $0.313 \text{ tons/day} \times 365 \text{ days/year} = 114 \text{ tons NaCl year}^{-1}$.

3.4.2. Oxygen and Other Gases in Water

Just like terrestrial counterparts, aquatic organisms (other than anaerobic microbes) need dissolved oxygen and other gases in order to survive. Additionally, the world's oceans "absorb" an estimated $1/4$ to $1/3$ of carbon dioxide emitted by human activity. If it were not for the ocean's ability to absorb carbon dioxide, an important greenhouse gas, global warming would proceed at an unprecedented rate (see also Chapter 24). The amount of gas that an aqueous solution can hold is dependent upon several variables, the most important of which is atmospheric pressure. Simply stated, increasing

INFORMATION BOX 3.1

Examples of Why Small Numbers are Important

- An AIDS virus is only 10^{-8} meters in size, or 0.00001 mm, yet it only takes one virus to have potentially devastating effects on the human immune system.

• From *Science*, 20 February 1991:

"In the end, after all the antibaryons had been consumed, one odd baryon out of 10 billion was left over. It was this tiny remnant that gave rise to all the planets, stars, and galaxies."

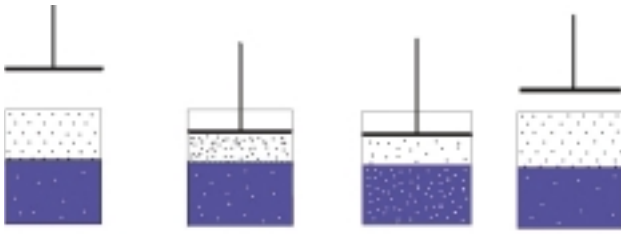


Figure 3.8 The solubility of oxygen in water under different atmospheric pressures.

atmospheric pressure causes a greater amount of gas to go into solution at a given temperature (Figure 3.8). Generally, increasing water temperature will result in an increased solubility of gas. This constant is otherwise known as “Henry’s Law” and is written as:

$$\rho = K'_c c \quad (\text{Eq. 3.1})$$

ρ = partial pressure of the gas in mmHg

c = concentration of gas in mmoles, mL, or mg L^{-1} at a constant temp

K'_c = the solubility factor, different for each gas

The constant K'_c is specific for every gas and solute at a given temperature (see also Chapter 7). There is a direct, linear relationship between the partial pressure and the concentration of gas in solution. For example, if the partial pressure is increased by $1/4$, the concentration of gas in solution is increased by $1/4$ and so on. This is because the number of collisions of gas molecules on the surface of the solute (water in this case) is directly proportional to increases or decreases in partial pressure. Since the concentration: pressure ratio remains the same, we can predict the concentration of gas in water under differing partial pressures. This relationship can be written as:

$$\frac{\text{Concentration1}}{\text{Pressure1}} = \frac{\text{Concentration2}}{\text{Pressure2}}$$

For example, 1 liter of water under 1 atmosphere of pressure, will contain 0.0404 grams of oxygen. What will the concentration of oxygen be if the partial pressure is increased to 15 atmospheres?

$$C1 = 0.0404 \text{ g O}_2/\text{1 liter solution}$$

$$P1 = 1 \text{ atm}$$

$$P2 = 15 \text{ atm}$$

$$C2 = ?$$

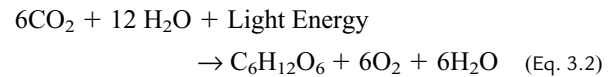
$$\frac{.0404 \text{ g O}_2}{1 \text{ atm}} = \frac{C2}{15 \text{ atm}}$$

$$C2 = (15 \text{ atm}) (0.0404 \text{ g O}_2 \text{ per 1 liter/1 atm})$$

$$C2 = 0.606 \text{ g O}_2$$

In any body of water, there are sources and sinks of dissolved oxygen. Sources include atmospheric re-aeration through turbulence; ripples and waves; and dams and waterfalls. Another potential source of dissolved oxygen is photosynthesis primarily by algae or submersed aquatic

vegetation. During photosynthesis, plants convert CO_2 into oxygen in the process outlined below.



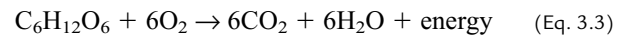
All natural waters also have sinks of dissolved oxygen, which include:

Sediment Oxygen Demand (SOD): Due to decomposition of organic material deposited on bottom sediments.

Biological Oxygen Demand (BOD): The oxygen required for cellular respiration by microorganisms.

Chemical Oxygen Demand (COD): The oxygen required for *all* organic compounds. Note that BOD is a subset of COD.

Respiration is the metabolic process by which organic carbon is oxidized to carbon dioxide and water with a net release of energy (see also Chapter 5). Aerobic respiration requires, and therefore consumes, oxygen.



This is, essentially, the opposite of photosynthesis. In the absence of light, the CO_2 collected by plants via photosynthesis during the day, is released back into the water at night, resulting in a net loss of dissolved oxygen. Depending upon the amount of nutrients, algae, and available light, this often results in large daily fluctuations in dissolved oxygen levels known as Diel patterns (Figure 3.9).

The implications of dissolved oxygen sinks and sources on aquatic organisms and overall water quality are crucial in determining whether or not a river, lake, or stream is polluted and to what degree. If dissolved oxygen sinks are greater than sources for extended periods of time, it is safe to assume some degree of contamination has occurred. Examples of anthropogenic wastes that can cause dissolved oxygen impairment of receiving waters are sewage (raw and treated, human and nonhuman), agricultural runoff, slaughterhouses, and pulp mills.

3.4.3 Carbon Dioxide in Water

Carbon dioxide only accounts for approximately 0.033% of the gases in earth’s atmosphere, yet is abundant in surface water. The biggest reason for the abundance of carbon dioxide in water is due to its relatively high solubility; almost 30 times that of oxygen. In the atmosphere, carbon dioxide is released when fossil fuels are burned for human uses, and as a result of large worldwide increases in the use of fossil fuels during the last century or so, the amount of carbon dioxide in the atmosphere has steadily increased. Carbon dioxide is currently rising at a rate of approximately $1 \text{ mg L}^{-1} \text{ year}^{-1}$ or about 40% since the beginning of the Industrial Revolution. Since carbon dioxide is a major greenhouse gas, changes in global climate may have long-term environmental consequences (Chapter 24).

At room temperature, carbon dioxide has a solubility in water of 90 ml^3 of carbon dioxide per 100 ml^3 of water.

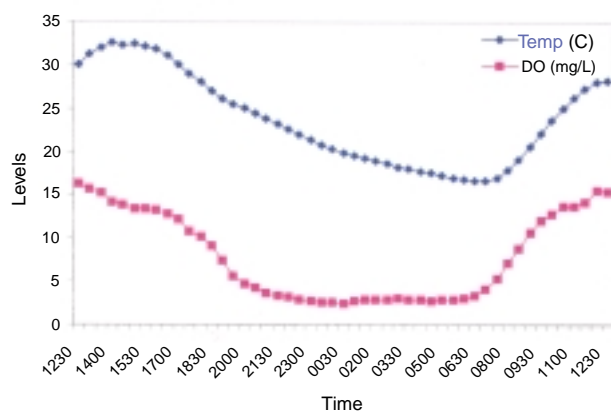
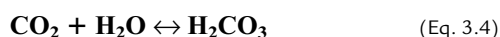
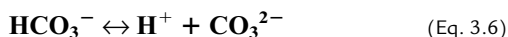
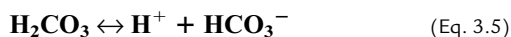


Figure 3.9 Diel pattern of temperature and dissolved oxygen in Rio de Flag, an effluent-dominated stream in Flagstaff, Arizona. **A.** Data was collected every 30 minutes over a 24-hour period on 08/12/03. **B.** Profuse growth of attached algae (“periphyton”) growing in the stream at the time. Photosynthesis and respiration by these algae likely contributed to the large swings in dissolved oxygen levels within the water over the 24-hour period. Photo courtesy D. Walker.

Carbon dioxide dissociates and exists in several forms in water. First, carbon dioxide can simply dissolve into water going from a gas to an aqueous form. A very small portion of carbon dioxide (less than 1%) dissolved in water is hydrated to form carbonic acid, (H_2CO_3). Equilibrium is then established between the dissolved carbon dioxide and carbonic acid.



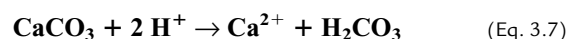
Carbonic acid, a very weak acid, is then dissociated in two steps.



As carbon dioxide is dissolved in water, equilibrium is eventually established with the carbonate ion (CO_3^{2-}). Carbonate, being a largely insoluble anion, then reacts with cations in the water, causing these cations to precipitate out of solution. As a result, Ca^+ and Mg^{2+} often precipitate as carbonates. Calcium carbonate (CaCO_3), otherwise known as limestone, has resulted in large deposits as a result of this process. As limestone is once again dissolved, carbon dioxide is released back into the atmosphere. In addition, several aquatic organisms, such as corals and shelled creatures such as clams, oysters, and scallops, are capable of converting the carbon dioxide in water into calcium carbonate.

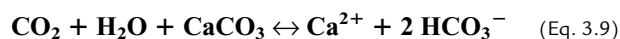
Diel fluctuations in oxygen and pH levels can occur during the day in waters where photosynthesis is taking place (see Figure 3.9). Algae and plants convert carbon dioxide into carbohydrates to be used in metabolic processes. In very productive waters, this process can leave bicarbonate or carbonate in excess, leading to increased pH levels. In the absence of adequate light for photosynthesis, respiration predominates, resulting in carbon dioxide once again being restored to the water resulting in decreased pH levels.

Calcium carbonate, while insoluble at neutral to basic pH levels, readily dissolves in acidic conditions. In the initial step, carbonate acts as a base resulting in calcium ions and carbonic acid. In the next step, carbonic acid is dissociated releasing carbon dioxide as a gas.

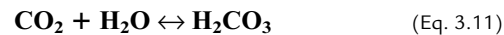


Rain is often slightly acidic due to the dissolution of atmospheric carbon dioxide. Recently, due to the burning of fossil fuels, other gases can also be dissolved in rain resulting in “acid rain.” Atmospheric pollutants responsible for acid rain include sulfur dioxide (SO_2) and nitrous oxides (NO_x). More than 2/3 of these pollutants come from burning fossil fuels for electrical power generation, and prevailing winds can result in acid rain being deposited far from original source. Acid rain has far-reaching environmental consequences including acidification of lakes and streams, making them uninhabitable by aquatic life; extensive damage to forests, plants, and soil; damage to building materials and automotive finishes; and human health concerns. However an amendment to the Clean Air Act, the **Acid Rain Program**, whose goal is to lower electrical power emissions of the pollutants causing acid rain, shows recent evidence of success, and lakes, rivers, and streams have responded favorably (see also Chapters 4 and 23).

In lieu of any anthropogenic acidification of rain or surface water, conditions often exist that can result in the dissolution of limestone:



The remaining reaction is a 3-step process:



This reaction can result in the formation of caves when naturally acidic rainwater reacts with a subterranean layer of limestone, dissolving the calcium carbonate and forming openings. As slightly acidic water reaches the cave ceiling, the water evaporates and carbon dioxide escapes. It is this reaction that is responsible for the many elaborate formations in cave ecosystems (Figure 3.10).

Total alkalinity is the total concentration of bases, usually carbonate and bicarbonate, in water and is expressed as mg/L of calcium carbonate. Analytically, total alkalinity is expressed as the amount of sulfuric acid needed to bring a so-

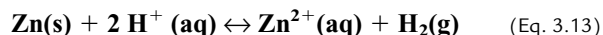


Figure 3.10 Cave formation in the Big Room, Carlsbad Caverns National Park, New Mexico. (<http://www.nps.gov/cave/home.htm>)

lution to a pH of 4.2. At this pH, the alkalinity in the solution is “used up,” and any further addition of an acid results in drastic decreases in pH levels. Total alkalinity, by definition, is the ability of a water body to neutralize acids. In other words, it is the “buffering capacity” of a water body, and it is influenced by the minerals in local soils. In areas of the northeastern U.S., where parent material contributes little to the total alkalinity in the water, the cumulative effects of acid rain have been most devastating and have extirpated aquatic life from several streams. Mining activity and pulp mills can also add to reductions in total alkalinity and subsequent decreases in pH. Stopgap measures in watersheds, lakes, or streams where alkalinity has been depleted include such drastic actions as dropping lime from helicopters to increase the buffering capacity for aquatic life.

3.5 OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions involve the transfer of electrons from one atom to another. Oxidation is defined as the loss of an electron from an atom, and reduction is the gain of an electron from an atom.



In the above example, the oxidation number of Zn has changed from 0 to +2, producing Zn^{2+} , and the oxidation number of H^+ has changed from +1 to 0, producing H_2 . In this reaction, Zn has been oxidized and H^+ has been reduced. Since Zn(s) was oxidized, it caused the reduction of $\text{H}^+(\text{aq})$ and is therefore the reducing agent. Likewise $\text{H}^+(\text{aq})$ caused the oxidation of Zn(s), making H^+ the oxidizing agent.

Loss of electrons from one substance must simultaneously be accompanied by the gain of electrons from another. Electrons are neither created nor destroyed in chemical reactions, and we can envision oxidation-reduction pairs. These

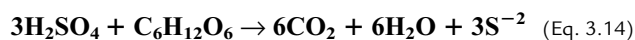
oxidation-reduction reactions are often referred to as **redox** reactions (see also Chapter 7). Just as the transfer of hydrogen ions determines the pH of a solution, the transfer of electrons between species determines the redox potential of an aqueous solution. Redox potential is also referred to as “ORP” for oxidation-reduction potential, and is measured in volts or *Eh* (1 volt = 1 *Eh*). ORP specifically measures the tendency for a solution to either gain or lose electrons when it is subject to change by the introduction of a new species. A solution with a higher ORP will have a tendency to gain electrons (*i.e.*, oxidize them) and a solution with a lower ORP will have a tendency to lose electrons to new species (*i.e.*, reduce them).

Whether a chemical species in solution is oxidized or reduced has a profound influence on biogeochemical cycling of metals, nutrients, salts, organic compounds, and so on. Examples of redox couplings of interest to water quality include the following (after Cole 1994):

REDOX COUPLE	VOLTS	DISSOLVED O ₂ (MG/L)
NO_3^- to NO_2^-	0.45–0.40	4.0
NO_2^- to NO_3^-	0.40–0.35	0.4
Fe^{+++} to Fe^{++}	0.30–0.20	0.1
SO_4^{--} to S^{--}	0.10–0.06	0.0

Redox reactions have an effect on bioavailability of nutrients. For example, iron exists either as particulate and oxidized ferric (Fe^{+++}), or the reduced and soluble ferrous (Fe^{++}). Phosphorous is an essential nutrient for plant and animal growth and under oxidizing conditions, is bound to ferric iron forming a ferro-phosphate complex that is biologically unavailable. If pollutants enter into a water body, dissolved oxygen may be depleted and reducing conditions prevail. Under these reducing conditions, iron loses its normally close association with phosphorous, with the latter becoming biologically available for algal growth sometimes forming noxious, and potentially toxic, blooms. Reducing conditions often prevail in the bottom of thermally stratified lakes and reservoirs, and phosphorous can accumulate leading to large growths of algae when the lake de-stratifies.

Methylation of mercury (addition of CH_3) also relies upon physical-chemical characteristics such as dissolved oxygen, pH, and ORP. Mercury is a metal that occurs naturally in the environment and has many different chemical forms. Methylmercury is the form of mercury that bioaccumulates (increases from one trophic level to the next by ingestion or absorption) and can cause mercury poisoning in wildlife and humans. Methylation of mercury can occur both abiotically and biotically by sulfate-reducing bacteria (SRB's) of the genera *Desulfovibrio* and *Desulfotomaculum*. SRB's require anaerobic and reducing conditions in their environment in order to reduce sulfate to sulfide. Specifically, they use sulfate as a terminal electron acceptor to break down molecular hydrogen or organic matter for metabolism through the following processes (see also Chapter 5).



Mercury (Hg) normally binds very tightly to organic matter. The above process is the method in which mercury can become de-coupled from organic matter and subsequently methylated via methyl transfer from cobalamin (vitamin B12) to Hg^{2+} .

3.6 LIGHT IN AQUATIC ENVIRONMENTS

Just as in terrestrial systems, light at the water's surface marks the beginning of photosynthesis or "primary production." Light is the driving force behind almost all metabolic processes in aquatic ecosystems. Light carries heat energy to be used in many chemical and biological processes, and can simultaneously regulate and/or damage, aquatic biota. Pollutants, especially suspended and dissolved substances, can have profound effects on both the amount of light available for photosynthesis and the heat energy needed for these processes.

3.6.1 Light Energy

Light contains differing amounts of energy, depending upon frequency and wavelength. Quantum theory states that electromagnetic energy, such as light, is transmitted in discrete amounts or "packets" called **quanta**. A single quanta (*i.e.*, "quantum") of electromagnetic energy is also referred to as a **photon**, and the energy carried by each photon is proportional to its frequency. The quantity of electromagnetic energy flow over time is measured as a rate, *i.e.*, quanta second^{-1} known as the **radiant flux of light**.

The arrangement of light based upon differing wavelengths, frequencies, and energies is described by *spectra*. For example, the spectrum formed by white light contains all colors and is therefore said to be continuous (Figure 3.11). Certain biological, chemical, and physical processes occur only at specific frequencies of spectra, some of which can be seen with the human eye and several of which cannot. Light that is divided over a certain range of spectra is divided by color and measured by its frequency in nanometers.

Light travels at $299,792 \text{ km second}^{-1}$. It takes approximately 400 trillion waves of red light at 750 nm to span the distance light travels every second. It takes almost twice as many violet waves, at 380 nm, to fill the same volume of a light second. The amount of radiation emitted by the sun that

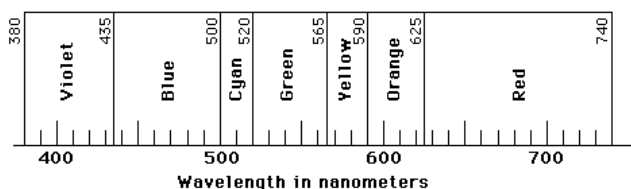


Figure 3.11 Wavelengths of light and associated spectra. (<http://hyperphysics.phy-astr.gsu.edu/hbase/vision/specol.html>)

reaches the earth's outer atmosphere is $1.94 \text{ calories cm}^{-2} \text{ minute}^{-1}$ and is known as the **solar constant**. The most common wavelength that makes it to our outer atmosphere is $\sim 480 \text{ nm}$.

Light wave frequency and energy are interrelated as explained by **Planck's equation**, which is expressed as:

$$E = h\nu \quad (\text{Eq. 3.15})$$

where:

E is the energy in a photon of light

h is Planck's constant of $6.6255 \times 10^{-34} \text{ joules second}^{-1}$

ν is the wave frequency

Frequency of a light wave is given by $\nu = c/\lambda$

where:

c is the speed of light ($3 \times 10^8 \text{ m/second}$), and

λ is the wavelength

For example, the frequency of red light (750 nm) is calculated from

$$\nu = \frac{3 \times 10^8}{7.5 \times 10^{-7}} = \frac{4.00 \times 10^{14}}{\text{second}^{-1} \text{ wavelengths light}}$$

Substituting this number into Planck's equation ($E = h\nu$), $26.5 \times 10^{-20} \text{ joules}$ are contained in a single photon of light. Compare this with the fact that it takes 6.024×10^{23} photons just to initiate a photosynthetic reaction (otherwise known as **Avogadro's number**). Thus, it can be seen that it takes a large amount of light energy to perform what we would consider a simple biological process. Photosynthetically active radiation, the spectrum of light needed for photosynthesis by most plants, is approximately 400 to 700 nm. Specific types of chlorophylls and accessory pigments in plants have narrowed the requirements of wavelength ranges. For example, chlorophyll *a*, a photosynthesizing pigment common to all algae, absorbs light in two peaks, 670–680 nm and again at 435 nm.

3.6.2 Light at and Below the Waters Surface

Several processes can affect both the intensity and quality of light reaching the earth's surface. One such process is simple scattering of light by particles in the atmosphere, including water vapor. Refraction of light occurs when the speed of light changes going from one medium, such as air, into another, such as water. Light can also be reflected off of a water surface due to several factors such as the incident angle of light, wave height and frequency, or the presence of ice. Another factor affecting light intensity is absorption due to the decrease in light energy by its transformation into heat. Both atmospheric gases and water can cause absorption.

Absorption (*i.e.*, "quenching") of light entering a body of water can be quantified using a **vertical absorption coefficient** expressed as:

$$k = \frac{\ln I_o - \ln I_z}{z}$$

where:

I_o is the natural log of the initial amount of light entering the water

I_z is the natural log of light remaining at any given depth

z is the thickness of the water in meters

The vertical absorption coefficient is somewhat analogous to the coefficient of extinction, except that the latter uses the base10 logarithm. The vertical coefficient of absorption is therefore 2.3 times the coefficient of extinction. Another important variable when considering the fate of light in water is **the total coefficient of absorption**, which is the sum of all factors leading to the intensity (or “extinction”) of light at any given depth. The total coefficient of absorption can be expressed as:

$$I_z = I_o e^{-kw} + I_o e^{-kp} + I_o e^{-kc}$$

where:

kw = the coefficient of absorption in pure water

kp = suspended particulate matter

kc = dissolved substances

Note that kp or kc can only be determined after filtration or centrifugation. The total coefficient of absorption is different for each body of water and is dependent upon the amount of dissolved or suspended material in the water. Dissolved substances are normally humic or fulvic acids, tannins, lignins, or anything that constitutes colored, dissolved, organic matter absorbing light strongly at relatively short wavelengths (e.g., blues and ultraviolet radiation < 500 nm). Suspended material includes fine clays, and phytoplankton, which absorb light evenly over the entire spectrum.

In standing water, vertical light penetration can be roughly estimated using a **secchi disk** which is standardized, 20-cm diameter, black and white, weighted disk lowered into the water using a calibrated line. The depth at which the disk almost, but not quite, disappears is recorded. This is known as the **secchi disk transparency** expressed as Z_{sd} . To be comparable, this has to be done between 10 am and 2 pm on any given day. Secchi disk depth is often mistakenly used as a proxy for primary production (the amount of standing algal biomass) in a water body. In reality there are many other mitigating factors besides algae that can cause either increases or decreases in transparency. The **photic zone** is the volume of water from the surface to where 99% of the light needed for photosynthesis has been extinguished. A very rough estimate of photic zone depth is anywhere from 2.7 to 3 times Z_{sd} .

3.7 OCEANS

3.7.1 Salts

The oceans are saline due to the constant input of dissolved salts leached from rocks and soils on land surfaces. These dissolved solids consist of many salts including sodium, calcium, and magnesium salts. There are several common methods of

determining total dissolved solids and/or salinity including electrical conductivity, density, light refraction, silver titration, and simple evaporation of a known volume. Each of these methods will provide a result that can be converted to a percentage, or more commonly parts per thousand, of salinity. Open ocean seawater will vary from 33 to 35 parts per thousand (ppt), while coastal waters may have less than 1 ppt.

3.7.2 Transport and Accumulation of Pollutants

The oceans tend to become the repository of many pollutants. Air pollution and water pollution often transport the compounds to the ocean through rain events or runoff. Historically, one of the most common mindsets was that the “solution to pollution is dilution.” Over time we have discovered that even the oceans are not vast enough to handle the volume of pollutants that can be discharged by human activities. In many cases, the effects of pollutants are so toxic that even vast dilution is not effective. In other instances we have found that filter-feeding organisms bioaccumulate toxic compounds that ascend food chains and can affect grazers and top carnivores, as well as humans consuming various seafoods. Mercury in swordfish and certain sharks is such an example.

3.7.3 Wave Morphology and Currents

Waves and currents move pollutants within surface water. This is especially critical in marine systems as we attempt to control and/or track pollution movement. Waves are typically the result of winds blowing across the surface of a body of water. As the air friction pushes against the water, small ripples form. Continued breezes push against the sides of each ripple providing additional energy. The tops of the ripples may blow off, forming whitecaps. This releases some of the energy, but more will continue with the bulk of the water below. Continued wind energy transferred to the waves can store enormous amounts of energy. The size of a wave is a function of the average velocity of the wind, the period of time it blows, and the distance of open water across which it blows. The distance over which blowing winds creates waves is called the **fetch**. Waves are usually described by the period (the time between two crests passing the same point), the wavelength (distance between two crests), and the wave height (vertical distance between a trough and the next crest).

Waves are important factors in the dispersion of pollutants, especially oil spills. Calm waters facilitate the recovery of oil and other floating pollutants. However, in cases where it cannot be collected, wave action can break up the thick mats of oil and spread the material so that bacterial degradation can break down the organic molecules. It will also allow the lighter fractions to volatilize.

Water motion in the oceans is a function of waves, which are wind driven, and currents, which are driven by a number of factors. The most important is the Coriolis effect caused by the spinning of the earth (see Chapter 4). However, wind, runoff from rivers, density differences from temperature or salinity extremes, and tidal fluctuations can all drive currents.

Currents are often compared to the circulatory system of a living organism. Trade winds will power currents that transport water and its constituents across vast distances along the surface. Cooling of surface waters in the high latitudes causes cold, dense water to sink into the depths, where it flows along the bottom until it upwells in lower latitudes to replace warmer surface waters that are blown away from coastlines. Tidal action will also drive currents in local situations.

Currents and waves effectively mix surface waters on a short time scale. Deep-water currents mix water on a much longer time scale. Together they effectively spread pollutants to every corner of the ocean. Water motion can be effectively measured in two ways. If the motion is fairly consistent in one direction, a current meter can be used to determine velocity. A more common situation is when water motion is not consistent, but varies in direction and speed in three dimensions over short periods of time. In this case, a better measure is to use a clod card. Clod cards consist of a block of calcium sulfate that slowly dissolves in water. The block is mounted on a card stock for easy attachment and handling. Its rate of dissolution can be measured by recording initial and final dry weights. These are normally used to compare two or more environments. The clod cards can be calibrated, if necessary, by placing controls in waters or tanks with known velocities of water motion.

3.8 LAKES AND RESERVOIRS—THE LENTIC SYSTEM

Lentic systems are closed ecosystems such as lakes. However, while lakes and reservoirs are relatively more “closed” than rivers and streams, they are far from isolated. Although some lakes and reservoirs have subterranean groundwater inputs, the majority of water entering them is a result of overland flow; therefore, lakes and reservoirs are reflections of all processes that have occurred in the watershed up to that point. Both natural and anthropogenic watershed influences can have profound effects on both water quality for human use and aquatic communities living within lentic systems.

3.8.1 Lentic Typology

There are several ways to classify lakes and reservoirs: by origin, ecoregion, shape and size, regimen of mixing, and stratification. Detail about every different type of lake or reservoir is beyond the scope of this chapter, and the reader is instead referred to any of several available limnological texts. Rather, this section will discuss the differences between two main types of lentic systems: lakes and reservoirs.

The main difference between lakes and reservoirs is that the former have natural origins, while the latter are manufactured by humans for anthropogenic needs. Both are lentic systems and therefore share some common attributes. Lakes are dominant where glaciers have scoured the landscape, as, for example, around the Great Lakes. In other cases, tectonic activity has formed rifts, allowing for the African Rift Lakes,

or some other depression has been made through natural causes and there is adequate ground or surface water inputs to fill these depressions. Reservoirs, on the other hand, are constructed where lakes are not in abundance and water is needed for human use. Reservoirs are often found in greater abundance in arid and semi-arid regions such as in the western U.S., where large natural lakes are not abundant. The large number of reservoirs built in arid regions often means sacrificing lotic habitats through either direct impoundment or some change in water chemistry caused by impoundment. Endemic aquatic organisms living in streams and rivers of the western U.S. are among the most endangered species on the planet due to impoundment of habitat and changes in environmental conditions below large dams.

Some of the major differences between lakes and reservoirs are given in Table 3.3. The arrows are either increasing or decreasing as they relate to either lakes or reservoirs. For example, lakes generally have a much smaller watershed area than reservoirs.

3.8.2 Trophic State

Material within lentic systems are generally classified as either **autochthonous** or **allochthonous** in origin. Allochthonous (from the Greek, meaning “other than from the earth or land itself”) material is everything that has been imported to the lentic system from somewhere else in the watershed. This material can be thought of in terms of *loading*. Autochthonous (from the Greek, meaning “of or from the earth or land itself”) material is that which is recycled within the lake or reservoir. Both sources play a role in a lentic system’s **trophic state**.

The trophic status of a lake or reservoir is largely a means to communicate the ecological condition of a water body. Trophic state is based upon the total weight of living biological material or biomass in a water body at a specific location and time. Time and location-specific measurements can be aggregated to produce waterbody-level estimations of trophic state. Trophic status is not equivalent to **primary production**, which is the rate of carbon fixed (usually expressed as g of C fixed day⁻¹ m⁻³). Trophic state, being a multidimensional phenomenon, has no single trophic indicator that adequately measures its underlying concept. Combining the major physical, chemical, and biological expressions of trophic state into a single index reduces the

TABLE 3.3 Comparisons of natural lakes and reservoirs.

VARIABLE	NATURAL LAKES	RESERVOIRS
Watershed Area	↓	↑
Maximum Depth	↓	↑
Mean Depth	↑	↓
Resident Time	↑	↓

TABLE 3.4 Trophic categories for lakes and reservoirs.

TROPHIC STATE	CHLOROPHYLL A ($\mu\text{g/L}$)	SECCHI DISK DEPTH (m)	TOTAL P ($\mu\text{g/L}$)	ATTRIBUTES
<30	<0.95	>8	<6	Oligotrophy: Clear water, dissolved oxygen throughout the year in the hypolimnion
30–40	0.95–2.6	8–4	6–12	Hypolimnia of shallower lakes may become anoxic
40–50	2.9–7.3	4–2	12–24	Mesotrophy: Water moderately clear; increasing probability of hypolimnetic anoxia during the summer.
60–60	7.3–20	2–1	24–48	Eutrophy: Problems with excessive primary production begin. Anoxic hypolimnia in stratified lakes/reservoirs.
60–70	20–56	0.5–1	48–96	Cyanobacteria dominate the phytoplankton. Increasing problems with anoxia.
>70	56–155	0.25–0.5	96–192	Hyper-eutrophy: Primary production limited only by light. Dense growths of algae and/or aquatic plants. Increasing prevalence of anoxia throughout the water column. Fish kills possible.
>80	>155	<0.25	192–384	Few aquatic plants or other forms of life. Sustained periods of anoxia.

variability associated with individual indicators and provides a reasonable composite measure of trophic conditions in a water body.

Several trophic state indices have been devised. The selection of which one to use depends upon several different chemical and physical parameters. One of the most-used trophic state indices for lakes is the **Carlson's TSI** (Carlson, 1977). Especially important are the nutrients phosphorous and nitrogen, both essential macronutrients for algal growth and primary production. Other variables used include measures of chlorophyll *a* and secchi disk depth. Chlorophyll *a* is a pigment common to all algae and gives a measure of standing biomass. Phosphorous is often the nutrient that is most "limiting" in natural waters (although nitrogen limitation also does occur). Carlson's TSI relies upon three variables—chlorophyll *a*, secchi disk depth, and total phosphorous—to determine trophic status of any water body that is phosphorous-limited. In the broadest sense, trophic status of a lake or reservoir is often divided into the categories presented in Table 3.4.

The advantage of a fixed boundary system is its easy application by managers and technical personnel with only limited limnological training. However, trophic terminology has a history of being mis-used. For example, deeming a lake as eutrophic does not automatically mean it has poor water quality. Although the concepts of water quality and trophic state are related, they should not be used interchangeably. Trophic state is an absolute scale that describes the biological condition of a body of water. The trophic scale is a division of variables used in the definition of trophic state and is not subject to change because of the attitude or biases of the observer. An oligotrophic or a eutrophic lake has attributes of production that remain constant no matter what the use of the water or where the lake is located. For the trophic state terms to have meaning, they must be applicable in any

situation and location, while keeping in mind that trophic status is just one of several aspects of the biology of the water body in question. Water quality, on the other hand, is a term used to describe the condition of a water body in relation to human needs or values. Quality is not an absolute; the terms "good" or "poor" water quality only have meaning relative to the attitude of the user. An oligotrophic lake might have "good" water quality for swimming, but have "poor" water quality for fishing. Confusion can ensue when trophic state is used to infer water quality.

3.8.3 Density and Layering

As light enters the water, different wavelengths are quenched exponentially (see 3.6.2). Wavelengths in the 620- to 740-nm range are absorbed first. This range also contains those wavelengths of light that carry the most amount of heat energy. The relative density of water is temperature-dependent. Water becomes increasingly dense down to about 4°C, at which point it becomes less dense (see 3.2.2). Thus, differential heating leads to differential vertical layering of the water column usually beginning in spring and early summer. The definitions of the various layers are given in Information Box 3.2. An example of thermal stratification in a lake is presented in Figure 3.12.

Interaction between the epilimnion and hypolimnion often results in the formation of autochthonous feedback mechanisms. In almost every case, anoxia within the hypolimnion mirrors epilimnetic production so that increases in trophic state result in increased hypolimnetic anoxia. Prolonged anoxia within the hypolimnion often results in the prevalence of reducing conditions (see Section 3.5). Under these reducing conditions, nutrients that would otherwise be bound to material within sediments become unbound and once again available for biological uptake. The density

INFORMATION BOX 3.2

Stratification of Lakes and Reservoirs

The uppermost layer is called the **epilimnion**, and is characterized by relatively warm water where most photosynthesis occurs. Depending upon environmental conditions, it is more oxygenated than layers below it. The middle layer is called the **metalimnion** and contains an area known as the *thermocline*. The thermocline is that area within the water column where the temperature gradient is the steepest. The metalimnion is that region surrounding the thermocline where the temperature gradient is steep compared to the upper and bottom layers. Due to the temperature gradient becoming increasingly steep within a correspondingly smaller volume of water, the thermocline becomes an infinitesimally small plane, whereas the metalimnion is a larger region encompassing the mean of the greatest rate of change. The **hypolimnion** is the bottom layer and is colder and denser than either the epilimnion or metalimnion. When a lake or reservoir is thermally stratified, the hypolimnion becomes largely isolated from atmospheric conditions and is often referred to as being stagnant. Additionally, the hypolimnion receives organic debris from the epilimnion, and as respiring bacteria begin the process of decomposition of this received material, consumption of dissolved oxygen (e.g., respiration) usually exceeds either production of oxygen from photosynthesis or atmospheric re-aeration. The epilimnion is often referred to as the **trophogenic** area of lentic systems, where mixing through wind and wave action as well as photosynthesis exceeds respiration, whereas the hypolimnion is referred to as the tropholytic region, where organic material is synthesized and mineralization by bacteria occurs.

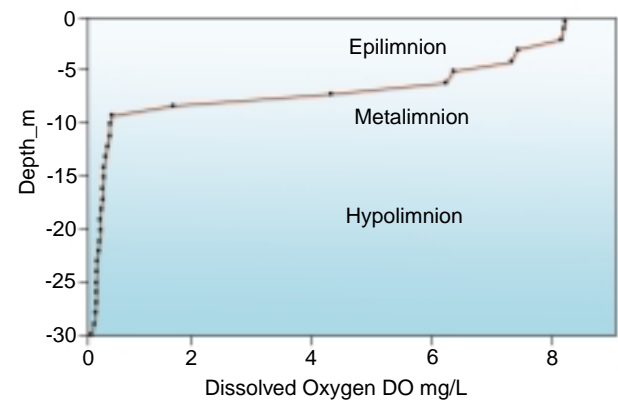
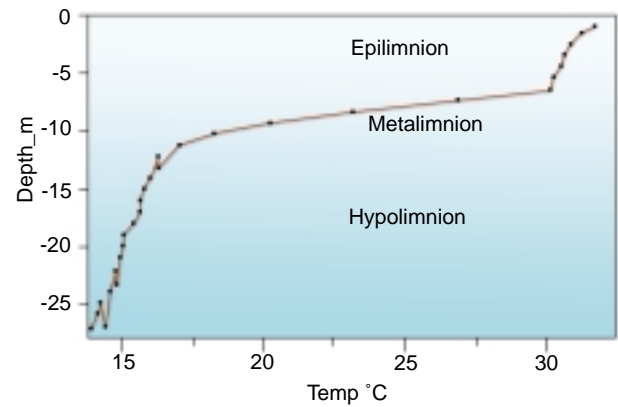


Figure 3.12 Thermal stratification in Lake Pleasant, Arizona. Data collected on 08/05/2003. The upper graph plots depth and temperature and the bottom graph depth and dissolved oxygen.

differences between the epilimnion and hypolimnion means that relatively few of these nutrients are available for uptake by phytoplankton until the lake or reservoir de-stratifies or “turns over,” which occurred when the epilimnion cools to a temperature similar to the hypolimnion (usually during the fall). Algal “blooms” or sudden increases in biomass of algae are common during this time.

Recycling of nutrients through the thermocline from the hypolimnion to the trophogenic epilimnion does occur, although this is relatively small compared to overall nutrient levels within the hypolimnion. Increases in algal biomass means that more organic material is available for transport back through the thermocline into the hypolimnion, adding to anoxia and the potential release of more nutrients from sediments, so that a positive feedback loop is established. This autochthonous cycling of nutrients can keep a lake or reservoir locked into a eutrophic state even after other sources of pollutants from the watershed have been reduced.

3.9 STREAMS AND RIVERS—THE LOTIC SYSTEM

Lotic systems consist of running water such as rivers or streams and are the great transporter of material to oceans, lakes, and reservoirs. Rivers and streams are also vulnerable to both natural and anthropogenic sources of pollution, and have a history of being used and misused.

3.9.1 Stream Morphometry

Stream morphometry was initiated by R.E. Horton and A.E. Strahler in the 1940s and 50s to find suites of holistic stream properties from the measurement of various attributes. This was designed to allow some type of classification system that could be used as a communicative tool for hydrologists (Figure 3.13).

The original idea was to develop a hierarchical classification system of stream segments. These segments were ordered numerically from headwaters so that individual tributaries at the headwaters were given the order of “1.” The joining of two 1st order streams were given the order of

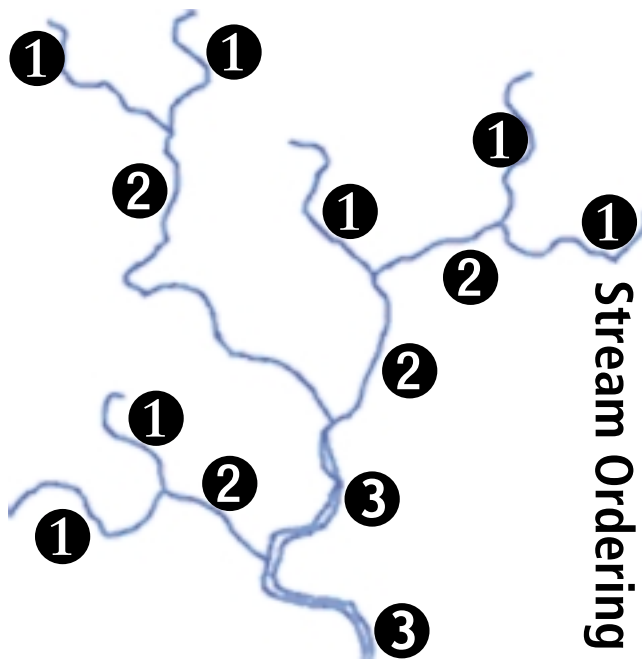





Figure 3.13 Example of stream ordering. Notice that it takes 2 stream orders of the same magnitude to increase downstream ranking. For example, the confluence of a 2nd order and a 1st order stream does not equal a third order, but the joining of two 2nd order streams does. (<http://www.cotf.edu/ete/modules/waterq/streamorder.html>)

“2” and the joining of two 2nd order streams, the order of “3,” and so on.

Horton found that the ratio between number of stream segments in one order and the next was consistently around three. This is called the **bifurcation ratio**. This ratio has also been discovered in the rooting system of plants, the branching structure of woody plants, leaf venation, and the human circulatory system.

ORDER	# OF SEGMENTS	BIFURCATION RATIO
1	30 	3.0
2	10 	3.3
3	3 	3.0

Horton called this association the **Law of Stream Numbers**, which is defined as the “morphometric relationship observed in the number of stream segments of a particular classification order in stream order branching.” Horton combined the information that he obtained to define the **Laws of Stream Lengths and Basin Areas**. The Law of Stream Lengths states that a geometric relationship exists between the numbers of stream segments in successive stream orders, whereas the Law of Basin Areas indicates that the mean basin area of successively ordered streams form a linear relationship.

A quantifiable measure of the morphometry of drainage networks is **drainage density**, which is the length of stream

channel per unit area of drainage basin expressed as:

$$\text{Drainage density (Dd)} = \frac{\text{stream length}}{\text{basin area}}$$

Drainage density is useful numerical measure of landscape dissection and runoff potential.

Rivers are often divided into relatively homogenous units or **reaches**. A river has distinct chemical, physical, and biological attributes, depending upon stream order and overall size of the channel. General physical characteristics based upon channel size are given in Table 3.5.

3.9.2 Stream Hydraulics

The flow of fluids is generally classified into two types: **laminar** and **turbulent**. For laminar flow, which occurs at lower velocities, the individual fluid (*e.g.*, water) molecules move uniformly in the direction of the mean gradient, with minimal mixing. Conversely, at higher velocities, the fluid molecules do not always move uniformly; instead, they may also cross the paths of other molecules, mixing and forming eddies. This is referred to as turbulent flow. The Reynolds number, a dimensionless parameter, is used to characterize conditions for which flow will be laminar or turbulent.

The volume of water flowing in a stream at a given time is referred to as the stream discharge. Discharge has units of volume per time (*e.g.*, cubic meters per second). It is calculated as: $Q = A * v$, where Q is discharge, A is cross-sectional area and v is velocity. The cross-sectional area of the stream, which has units of length squared, is controlled by the shape and size of the channel and the height of water in the channel. This latter term is often referred to as the stream stage. The velocity (units of length per time) of water in a stream is controlled by the gradient (slope) of the stream and roughness of the stream channel surfaces. Water velocities are generally not uniform across the stream cross-section. Rather, the highest velocities typically occur in the center of the channel just below the surface, and the lowest velocities occur along the channel surfaces (where friction is greatest).

3.10 GROUNDWATER—WATER IN THE SUBSURFACE

Water in the subsurface serves as a critical resource for human consumption, both directly and indirectly (see Chapter 17). Groundwater resources serve as one of the two primary sources of potable water supply in the world (the other being surface water). In addition, water in the soil profile supports plant life, upon which humans are dependent in several ways. Water is also central to the transport and fate of contaminants in the subsurface. We will examine the distribution and movement of groundwater in this section. The impact of water flow on transport of contaminants in the subsurface is discussed in Chapters 6 and 17.

TABLE 3.5 Properties of stream channels.

CHANNEL SIZE	PHYSICAL CHARACTERISTICS	ORDER
<i>Small</i>	Cobbles (>64 mm dia.) And boulders (>256 mm dia.) Dominate the substrate. Pools form behind rocks or logs (step-pool formations) Relatively steep gradients (2° to 20°) Banks composed of bedrock, boulders, and roots. Highly erosional areas.	Low
<i>Intermediate</i>	20–30 m max. width Dominated by pool-riffle-bar units Riffles are zones of relatively shallow, rapid flow Rapids, cascades, and glides (extended riffles) may be prominent. Major pool types include <i>backwater</i> (formed from either obstructions in the main channel or from periodic flooding of banks), <i>dammed</i> (found upstream of boulder lies and gravel bars), and <i>scour</i> (where flow converges past an obstruction).	Intermediate
<i>Large</i>	Dominated by pool-riffle sequences, bar formations, and meanders. Reach gradient largely determined by valley gradient. Transport of sediment may increase <i>sinuosity</i> . Sinuosity is defined as river length/valley length. Braided channels may form when the river can no longer carry its sediment load. Increased deposition of sediment in large channels.	High

From Callow & Petts, 1992.

3.10.1 Water in the Subsurface

We can observe a cross-section of water distribution in the subsurface by drilling a borehole or excavating a pit. A schematic of a typical subsurface profile was presented in Figure 2.1. The vadose zone, also known as the zone of aeration or unsaturated zone, represents a region extending from near the ground surface to a water table. The water table is defined as a water surface that is at atmospheric pressure. In the soil and vadose zones, all pores are usually not filled with water; many pores will also contain air. In such cases, the porous medium is considered to be unsaturated. Water pressure in the soil and vadose zones is less than atmospheric pressure ($P < 0$). The thickness of the vadose zone varies from a meter or less in tropical regions to a few hundred meters in arid regions, depending upon the climate (e.g., precipitation), soil texture, and vegetation (see also Chapter 2).

Water stored in the soil and vadose zones is retained by surface and capillary forces acting against gravitational forces. Molecular forces hold water in a thin film around soil grains. Capillary forces hold water in the small pores between soil grains. Gravity forces are not sufficient to force this water to percolate downward. Thus, there is very little movement of water in the vadose zone when water contents are relatively low. For higher water-content conditions,

some of the water is free to move under the influence of gravity. When this occurs, water movement would generally be vertically downward. If this water moves all the way to the water table, it serves to replenish (or recharge) groundwater. The **capillary fringe** is the region above the water table where water is pulled from the water table by capillary forces. This zone is also called the **tension-saturated zone**. The thickness of this zone is a function of grain-size distribution and varies from a few centimeters in coarse-grained soils to a few meters in fine-grained soils. The water content in this zone ranges from saturated to partially saturated, but fluid pressure acting on the water is less than atmospheric pressure ($P < 0$).

The region beneath the water table is called the saturated or phreatic zone. In this zone, all pores are saturated with water and the water is held under positive pressure. Because all pores are filled with water, soil-water content is equal to porosity, except when liquid organic contaminants are also present in the pore spaces (see Chapter 17). The water in the saturated zone is usually referred to as groundwater. Water movement in the saturated zone is generally horizontal. Specific sections of the saturated zone, particularly those comprised of sands and gravels, are called aquifers, which are geologic units that store and transmit significant quantities of groundwater.

3.10.2 Principles of Subsurface Water Flow

Water at any point in the subsurface possesses energy in mechanical, thermal, and chemical forms. The energy status of water, for example the effort required to move water from one point to another, is a critical aspect of quantifying water flow. For groundwater flow, the contributions of chemical and thermal energies to the total energy of water are generally relatively minor and thus are usually ignored. Therefore, we consider water flow through porous media to be primarily a mechanical process. Fluid flow through porous media always occurs from regions where energy per unit mass of fluid (fluid potential) is higher, to regions where it is lower.

From fluid mechanics, the mechanical energy of water at any point is composed of the kinetic energy of the fluid, the potential (or elevation) energy, and the energy of fluid pressure. For water flow in porous media, kinetic energy is generally negligible because pore-water velocities are usually small. Thus, total energy of water is considered to consist of potential and pressure energies.

The potential or elevation energy results from the force of gravity acting on the water. In the absence of pressure energy considerations, water always flows from regions of higher elevation potential to lower. This is why surface water flows “downhill.” Similarly, groundwater usually flows downward from higher elevations (underneath mountain peaks) to lower elevations (underneath the valley floor).

In the vadose zone, the pressure potential is negative, indicating that energy is required to “pull” water away from the soil surfaces and small pores. In the saturated zone, the pressure potential is positive due to the pressure exerted by

overlying water. The water pressure increases with depth in the saturated zone. This condition occurs in all water bodies—including swimming pools—which is manifested by the increasing pressure one feels on their sinuses and eardrums, as one swims deeper below the surface.

The energy potentials are commonly expressed in terms of length to simplify their use. In length terms, the energy potentials are referred to as “heads.” The total energy potential head for water is called the **hydraulic head**; sometimes, particularly for vadose-zone applications, it is called the **soil-water potential head**. The equation we use to relate the hydraulic head (h) to its two parts, elevation head (z) and pressure head (Ψ), is: $h = \Psi + z$. Each head has a dimension of length (L) and is generally expressed in meter or feet.

Hydraulic head measurements are essential pieces of information that are required for characterizing groundwater flow systems (*i.e.*, direction and magnitude of flow), determining hydraulic properties of aquifers, and evaluating the influence of pumping on water levels in a region. Piezometers are used to measure the hydraulic head at distinct points in saturated regions of the subsurface. A piezometer is a hollow tube or pipe drilled or forced into a profile to a specific depth. Water rises inside the tube to a level corresponding to the pressure head at the terminus. The level to which water rises in the piezometer with reference to a datum such as sea level is the hydraulic head (Figure 3.14).

The relationship between the three head components is illustrated in a piezometer in Figure 3.14. The value of z represents the distance between the measurement point in the profile and a reference datum. Sea level is often taken as

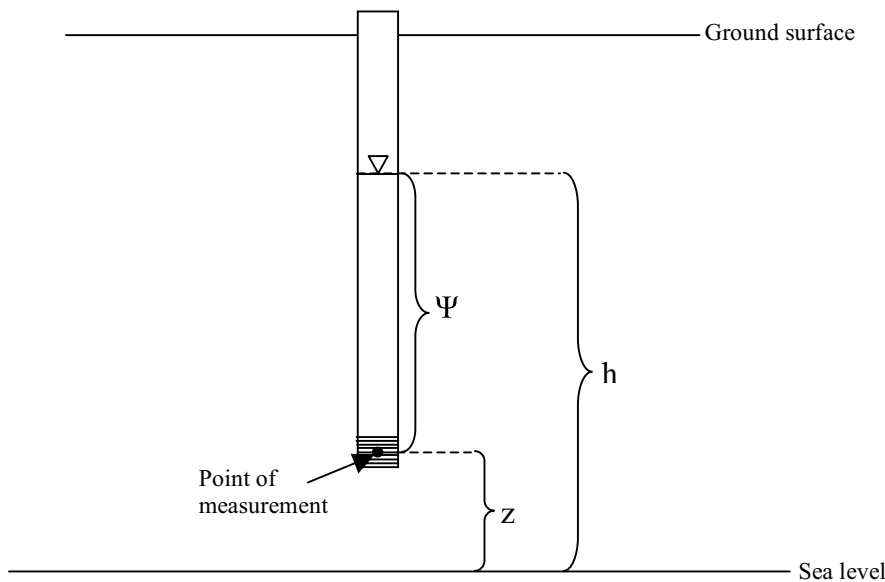


Figure 3.14 Concept of hydraulic head (h), elevation head (z) and pressure head (Ψ) in a piezometer. The cross-hatched section at the bottoms of the tube (terminus) represents the screened interval, which allows water to flow into the piezometer. Water level is denoted by the “▽” symbol. From Yolcubal et al., 2004.

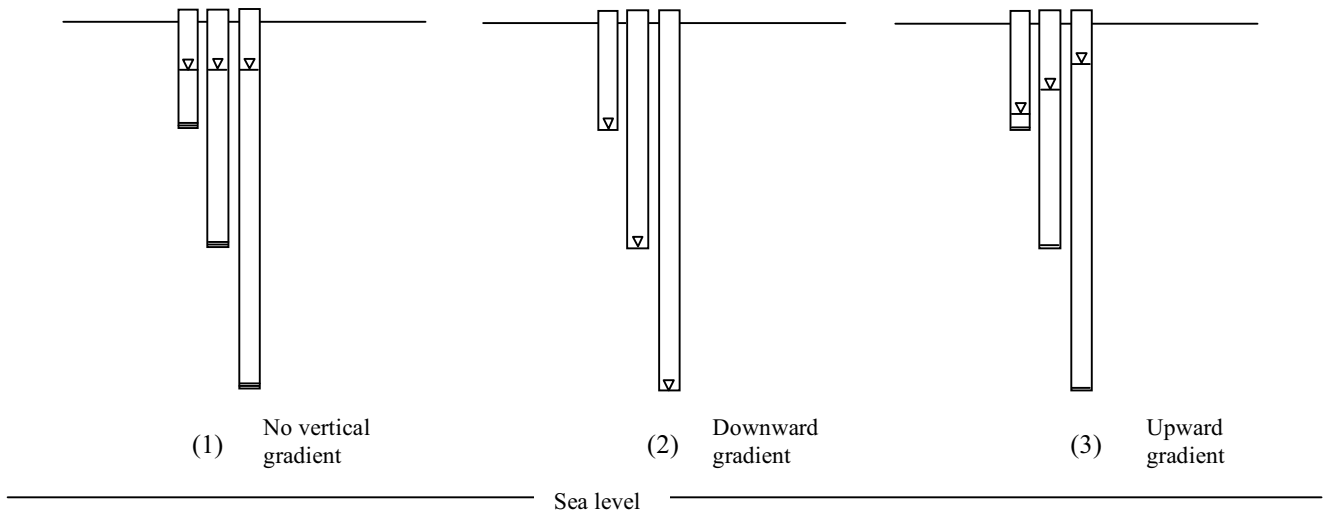


Figure 3.15 Three hypothetical situations for vertical hydraulic gradient water level is denoted by the “∇” symbol. From Yolcubal et al., 2004.

the reference point where $z = 0$, although some people use the elevation of land surface as the reference datum. The value of Ψ represents the distance between the measurement point and the water level in the well. The value of h represents the elevation of water from the reference datum. This basic hydraulic head relationship is essential to an understanding of groundwater flow. Water flow in porous media always occurs from regions in which hydraulic head is higher to regions in which it is lower.

Water level measurements in a network of production or monitor wells are used to define the potentiometric (or water table) surface of regional ground water. Knowledge of this surface is required to define hydraulic gradients and flow directions. Data from piezometers terminating in depth-wise increments provide information about the vertical flow direction of water in saturated regions (Figure 3.15). In the first (left side) diagram, the water level is uniform, indicating no vertical flow. In the second (middle) diagram, the water level is highest in the shallowest piezometer and lowest in the deepest one, indicating downward flow. The reverse is true for the third (right side) diagram.

3.10.3 Darcy's Law

In 1856, a French hydraulic engineer, Henry Darcy, established a relationship that bears his name to this day. The relationship is based on studies of water flow through columns of sand, similar to the schematic shown in Figure 3.16. In Darcy's experiment, the column is packed with sand and plugged on both ends with stoppers. Water is introduced into the column under pressure through an inlet in the stopper and allowed to flow through it until all the pores are fully saturated with water and inflow and outflow rates are equal. Water pressures along the flow path are measured by the manometers installed at the ends of the column.

In his series of experiments, Darcy studied the relationship between flow rate and the head loss between the inlet and outlet of the column. He found that:

1. The flow rate is proportional to the head loss between the inlet and outlet of the column:

$$Q \propto (H_a - h_b)$$

The flow rate is inversely proportional to the length of flow path:

$$Q \propto \frac{1}{dl}$$

2. The flow rate is proportional to the cross-sectional area of the column:

$$Q \propto A$$

Mathematically, these experimental results can be written as:

$$Q = KA \left[\frac{h_a - h_b}{\Delta l} \right] = KA \left[\frac{\Delta h}{\Delta l} \right]$$

where:

Q = flow rate or discharge [$L^3 T^{-1}$]

A = cross-sectional area of the column [L^2]

$h_{a,b}$ = hydraulic head [L]

dh = head loss between two measurement points [L]

dl = the distance between the measurement locations [L]

dh/dl = hydraulic gradient []

K = proportionality constant or hydraulic conductivity [$L T^{-1}$]

We can rewrite Darcy's Law as:

$$\frac{Q}{A} = q = \frac{K dh}{dl}$$

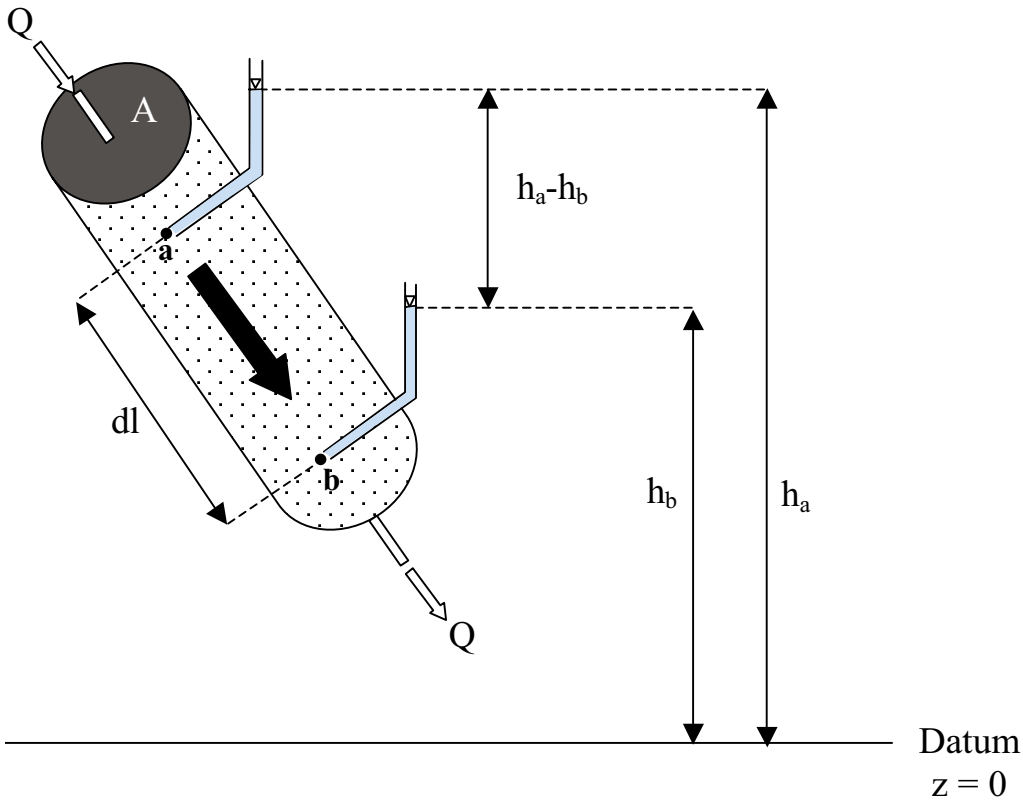


Figure 3.16 Schematic of Darcy's experimental apparatus (original apparatus was vertically oriented). From Yolcubal et al., 2004.

where q is called specific discharge or Darcy velocity with units designated as $[L T^{-1}]$. This is an apparent velocity because Darcy velocity represents the total discharge over a cross-sectional area of the porous medium. Cross-sectional area includes both void and solid spaces; however, water flow occurs only in the connected pore spaces of the cross sectional area. Therefore, to determine the actual mean water velocity, specific discharge is divided by the porosity of the porous medium: $v = q/n$, where v is the pore-water velocity or average linear velocity. Pore-water velocity is always greater than Darcy velocity.

3.10.4 Hydraulic Conductivity

The proportionality constant in Darcy's law, which is called **hydraulic conductivity (K)** or **coefficient of permeability**, is a measure of the fluid transmitting capacity of a porous medium and is expressed as:

$$K = \frac{k\rho g}{\mu}$$

where:

- k is the intrinsic or specific permeability $[L^2]$
- ρ is the fluid density $[M L^{-3}]$
- g is the acceleration due to gravity $[L T^{-2}]$
- μ is the dynamic viscosity of the fluid $[M T^{-1} L^{-1}]$

Hydraulic conductivity has a dimension of velocity $[L T^{-1}]$, and is usually expressed in $m s^{-1}$, $cm s^{-1}$, or $m day^{-1}$ in SI units, or $ft s^{-1}$, $ft day^{-1}$, or $gal day^{-1} ft^{-2}$.

As indicated by the equation above, hydraulic conductivity depends on properties of both the fluid and porous medium. The two fluid properties are density and dynamic viscosity. Intrinsic permeability is a property that in most cases depends solely on the physical properties of the porous medium. This relationship can be illustrated using the expression called the **Hazen approximation**:

$$k = C(d_{10})^2$$

where:

- C is a shape factor [dimensionless]
- d_{10} is the effective grain diameter $[L]$

C is a constant that represents the packing geometry, grain morphology (size and shape), and grain-size distribution of the porous medium. The value of C ranges between 45 for clays and 140 for sand. A value of $C = 100$ is often used as an average. d_{10} is the diameter for which 10% (by weight) of the sample has grain diameters smaller than that diameter, as determined by sieve analysis. The Hazen approximation is applicable to sand with an effective mean diameter between 0.1 and 3.0 mm. Intrinsic permeability (k) has dimensions of square feet (ft^2), square meter (m^2), or square centimeter (cm^2).

As noted above, porous-media properties that control K include pore size, grain-size distribution, grain geometry, and packing of grains. Among those properties, the influence of grain size on K is dramatic, since K is linearly proportional to the square of grain diameter. The larger the grain diameter, the larger is the hydraulic conductivity. For example, hydraulic conductivity of sands ranges from 10^{-4} to 10^{-1} cm s^{-1} , whereas the hydraulic conductivity of clays ranges from 10^{-9} to 10^{-7} cm s^{-1} . The values of saturated hydraulic conductivity vary by several orders of magnitude, depending on the material. The range of values of hydraulic conductivity and intrinsic permeability for different media is illustrated in Figure 3.17.

In the vadose zone, hydraulic conductivity is not only a function of fluid and media properties, but also the soil-water content (θ), and is described by the following equation:

$$K(\theta) = K k_r(\theta)$$

where:

- K(θ) is the unsaturated hydraulic conductivity
- K is the saturated hydraulic conductivity
- $k_r(\theta)$ is the relative permeability or relative hydraulic conductivity

Relative permeability is a dimensionless number that ranges between 0 and 1. The $k_r(\theta)$ term equals 1 when all the pores are fully saturated with water, and equals 0 when the porous medium is dry. Unsaturated hydraulic conductivity is always lower than saturated hydraulic conductivity.

Unsaturated hydraulic conductivity is a function of soil-water content. As the soil-water content decreases, so does K(θ). In fact, a small drop in the soil-water content of a porous medium, depending upon its texture, may result in a dramatic decrease (e.g., $10^3, 10^6$) in the unsaturated hydraulic conductivity. As we discussed earlier, the hydraulic conductivity of

sands is always greater than that of clays for saturated porous media. However, in the vadose zone, this relationship may not always hold true. For example, during drainage of a soil, larger pores drain first and the residual water remains in the smaller pores. Since sand has larger pores than clay, it will lose a greater proportion of water for a given suction. Consequently, at relatively low soil-water contents (high suctions), most of the pores of a sand will be drained, while many for a clay will remain saturated. Therefore, the unsaturated hydraulic conductivity of a clay unit may become greater than that of a sand unit at lower soil-water contents.

Hydraulic conductivity is a critical piece of information required for evaluating aquifer performance, characterizing contaminated sites for remediation, and determining the fate and transport of contaminant plumes in subsurface environments. For example, for water management issues, one needs to know the hydraulic conductivity to calculate the water-transmitting and storage capacities of the aquifers. For remediation applications, knowledge of K distribution of contaminated soils is necessary for calculating plume velocity and travel time, to determine if the plume may reach a downgradient location of concern. Hydraulic conductivity can be measured in the laboratory as well as in the field. Laboratory measurements are performed on either disturbed or undisturbed samples that are collected in the field. Laboratory measurements are relatively inexpensive, quick, and easy to make compared to field measurements. They are often used to obtain an initial characterization of a site before on-site characterization is initiated. However, measurements made for a sample represent that specific volume of media. A single sample will rarely provide an accurate representation of the field because of the heterogeneity inherent to the subsurface. Thus, a large number of samples would usually be required to characterize the hydraulic conductivity distribution

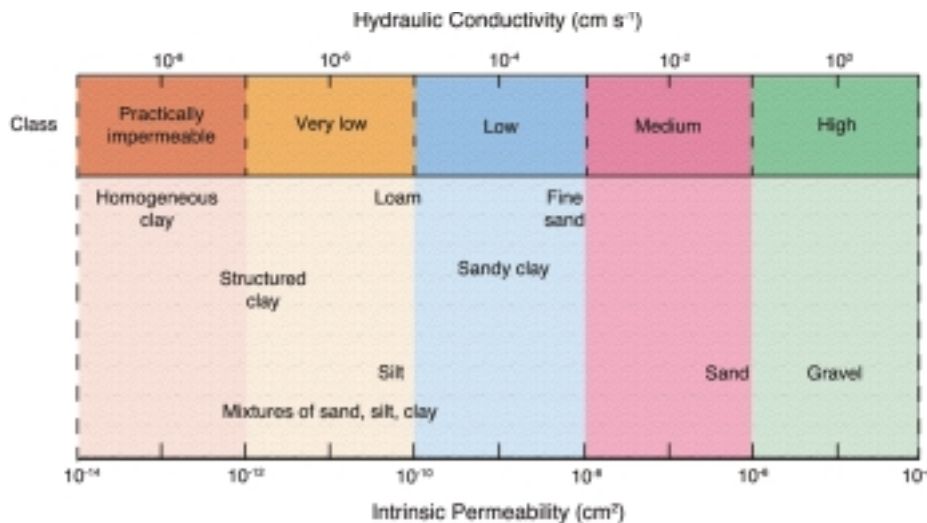


Figure 3.17 Hydraulic conductivity and permeability at saturation. (Adapted from Klute, A., and Dirksen, C. [1982] *Methods of Soil Analysis. Part I— Physical and mineralogical methods.* Soil Science Society of America, Madison, WI).

present at the site. Thus, field tests, while more expensive, are generally preferred to characterize large sites.

3.11 A WATERSHED APPROACH

Strictly defined, a watershed is a bound hydrologic unit where all drainages flow to a common water source. Referring back to the section on stream order, we can see that a watershed encompasses all stream orders from beginning to end. No matter where one goes on the earth (excluding the oceans), that person would be in a distinct watershed. Watersheds are usually delineated by sharp gradients and precipitation or snowmelt flows along one side of the gradient or the other, depending upon local topography and natural hydrology.

Increasingly, resource managers are using watersheds as the unit of measure for management and delineation purposes on a landscape scale. In hydrologic terms, it makes perfect sense to focus management efforts in these terms, because a land use activity in one part of a watershed often has an effect on downstream areas. The more traditional approach of addressing specific sources of pollution in a specific area has been successful in addressing problems that are readily noticeable; however, this approach has met with limited success in addressing the chronic and subtle stressors that often contribute to impairment within a watershed. A watershed framework is better able to capture these subtle changes over time.

It's important to understand that watersheds, and the organisms they contain, pay no attention to human-imposed

political boundaries. Natural physical, chemical, and biological processes within watersheds provide civilization-sustaining benefits when functioning properly. Unfortunately, the same civilization to which watersheds provide these benefits is often the source of impairment and disruption of natural processes within them. Acknowledging this fact while understanding that political boundaries do exist is a necessary prerequisite toward cooperative management of the world's most precious natural resource.

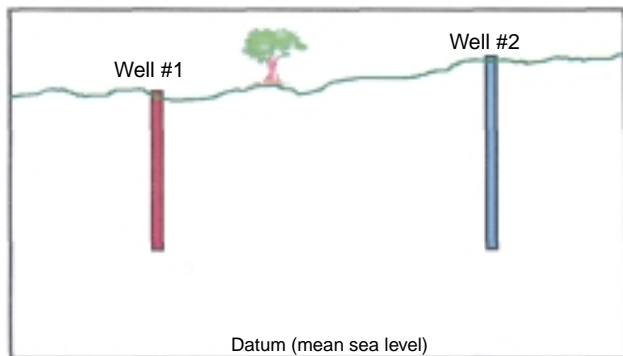
While water within watersheds follows the physicochemical "laws" previously described in this chapter, watershed management is equal parts hydrology and social science. Watershed management acknowledges that humans are a part of, not separated from, watershed processes and functioning. Watershed management, as a component of ecosystem management, tries to unify communities, managers, water quality experts, and as many stakeholders as possible, with the overall goal of increasing or sustaining water quality over large geographic areas for the common good of not only affected communities, but also of the watershed itself.

This ideology is far from revolutionary, and perhaps the best definition of a watershed was by the geologist, explorer, and teacher John Wesley Powell, who stated over 100 years ago that:

"A watershed is that area of land, a bounded hydrologic system within which all living things are inextricably linked by their common water course and where, as humans settled, simple logic demanded that they become part of a community."

QUESTIONS AND PROBLEMS

1. A. Determine pressure head (Ψ), elevation head (z), and hydraulic head (h) for both wells.
B. Calculate the hydraulic gradient.
C. Does groundwater flow from well #1 to #2, or from #2 to #1?



The horizontal distance between the wells is 250 meters.
Well 1: The elevation at the ground surface is 100 m; the measured water level in the well is 40 meters below the ground surface. The well casing length is 60 m.

- Well 2. The elevation at the ground surface is 115 m; the measured water level in the well is 50 meters below the ground surface. The well casing length is 80 m.
2. Why is hydraulic conductivity a function of the fluid as well as the porous medium? Is the conductivity for water greater than or less than that for air (for a given porous medium)?
 3. Water has been described as a universal solvent. Describe three properties of water that account for its ability to dissolve so many types of compounds.
 4. Describe some physical, chemical, and biological characteristics within the epilimnion and hypolimnion of a thermally stratified lake.
 5. For the temperatures and pressures given below, determine if water will be in a solid, liquid, or gaseous state (or some combination thereof).
 - a. 219 ATM and 0.0000098°C
 - b. 100 ATM and 100°C
 - c. 1 ATM and 373°C
 - d. 0.006 ATM and 0.01°C

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