Chapter 13
Mineral Water: Essential to Life, Health, and Wellness

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Abstract Mineral water is the natural water that is essential to life, health, and wellness and comes from aquifers, either superficial or underground, through pumping, deep wells, and springs. Mineral water is an essential constituent of the human body. Mineral water is rich in minerals and is used as it is or after undergoing purification. In general, mineral water for human consumption undergoes physical and chemical treatments, microbiological control, and monitoring too to ensure maximum purity. It is known for centuries that minerals existing in solution into drinking water are essential for humans, animals, and plants, different minerals having different functions. Water is an essential constituent of the human body, and minerals condition the physical, chemical, and physicochemical properties of the drinking mineral water that should be safe not only chemically but microbiologically too. Water quality issues are a major challenge that humanity is facing in the twenty-first century. The chapter reports basic and actual information on mineral water as an essential constituent of the human body and health conditioner, as well as on sources and resources, on sanitary safety, and on typologies and functions.

13.1 Background Data on Mineral Water

Water quality issues are a major challenge that humanity is facing in the twenty-first century. Schwarzenbach et al. (2010) have reviewed the main groups of aquatic contaminants, their effects on human health, and approaches to mitigate pollution of freshwater resources. Emphasis is placed on chemical pollution, particularly on inorganic and organic micropollutants including toxic metals and metalloids, as

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well as a large variety of synthetic organic chemicals. Geogenic contamination of underground waters and mining operations' contamination of surface waters are important sources of inorganic pollutants.

The so-called waterborne diseases are due to chemical contaminants and to pathogens present in drinking water. Climate changes, increasing water temperature, severe rainfall, and flooding events will favor the spread of waterborne diseases, in particular infectious disease outbreaks, such as yellow fever, malaria, and dengue (Myers and Patz 2009; WHO 2007).

Mineral waters can be classified according to their origin:

1. Meteorological – those existing in superficial aquifers produced by rain, snow, and de-icing
2. Juvenile – those that see daylight when surfacing
3. Fossil – those existing in confined underground aquifers, either in continental areas or in sea areas

There are different categories of waters intended for human consumption, such as *natural mineral waters* and *spring waters*:

1. Natural mineral waters may be distinguished from ordinary drinking mineral water by their *purity* at source and their *constant level of minerals*; spring waters are intended for human consumption in their natural state and are bottled at the source.
2. Directive 2009/54/EC regulates the marketing and exploitation of natural mineral waters. Certain provisions of this Directive are also applicable to spring waters such as the microbiological requirements and labelling requirements.
3. Commission Directive 2003/40/EC of 16 May 2003 establishes the list, concentration limits, and labelling requirements for the natural mineral waters and the conditions for using ozone-enriched air for the treatment of natural mineral waters and spring waters.
4. Natural mineral water exploration and exploitation is conditioned to an authorization procedure carried out by the Competent Authorities of the EU Member States.

13.2 Mineral Water: Sources and Resources

On the one hand, the current "best guess" for liquid water appearance on Earth, in the so-called primitive oceans, was around 4.4 Ga years ago, the solar system being formed at around 4.6 Ga years ago and the Earth being formed at around 4.5 Ga years ago. Such water would have resulted from both impacts on Earth of *icy* planetesimals similar in composition to comets and the asteroids in the outer edges of the asteroid belt and from the vast cloud of dust and gas remaining after the Sun's formation, called the *solar nebula* (Wu et al. 2018).

Also, Moon-forming impact at around 4.5 Ga ago between the two young planets Earth and Theia would have vaporized much of Earth's crust and upper mantle and created a rock vapor atmosphere around the Earth which is unique among the rocky planets in the solar system in that it is the only planet known to have oceans of liquid water on its surface.

In the case of Earth's oceans, the deuterium-to-hydrogen or ^{2}H-to-^{1}H ratio is close to what is found in asteroids, the reason why scientists have long thought that most earthly water came from an asteroid bombardment in the days of the early solar system.

On the other hand, the current "best guess" for the earliest appearance of life on Earth is around 4–3.8 Ga in the transition of the Hadean geological eon (~4.5 Ga–4.0 Ga) to the Archean geological eon, and the first life forms of single-celled organisms most probably based on RNA may have been developed in undersea alkaline vents, this being a hypothesis like others referred to in Chap. 7 of this book.

In the late Hadean, the Earth's atmosphere consisted largely of water vapor, nitrogen, and carbon dioxide, with smaller amounts of carbon monoxide, hydrogen, and sulfur compounds (Kasting 1993; Genda 2019).

The appearance of oxygen in the atmosphere probably at around 2.3 Ga years ago is mainly the result of photosynthesis in cyanobacteria – the only bacteria that produce oxygen as a byproduct of their metabolism, using light, water, and carbon dioxide to produce oxygen and biomass. It was not until these creatures appeared on Earth that oxygen was found in the Earth's atmosphere, which played a key role in the evolution of single-celled organisms to multicelled organisms. To build up one complex multicellular organism, energy is needed, and the oxygen would be the trigger to get such energy.

About 71% of the Earth's surface is covered by water with a total estimate of 1.4×10^9 km^3. The Earth's surface oceans appear to have existed since very early in the Earth's history, perhaps even since the Earth's formation, and the presence of oceans distinguishes Earth from other planets in the solar system. However, the mass of the Earth's oceans (Moce = 1.4×10^{21} kg) is only 0.023 wt% of the planet's total mass (ME = 6.0×10^{24} kg). Even if the water in the Earth's interior (the mantle and core) is taken into account, the mass fraction of water does not exceed 2 wt% of the total planetary mass (Genda 2016). The water content in the Earth's mantle can be estimated to be from one to ten times the present ocean mass.

The suitable distance of Earth from the Sun (the central star of the solar system) is the most important factor determining the stability of liquid water on the Earth's surface, shorter distance would cause water vaporization, and longer distance would cause water congelation. The adequate distance of Earth from the Sun and a suitable amount of greenhouse gases in the Earth's atmosphere have made this planet habitable. H_2O molecules are expected to be abundant in the solar system because hydrogen is the most abundant chemical element in the solar system.

From outer space, the Earth looks like a "blue planet" because most of its surface is covered by water, particularly in the oceans.

Only 2.5% of that water is fresh, and most of that lies frozen and inaccessible in the icecaps and Greenland, leaving less than 1% of fresh water accessible in lakes, river channels, and underground. A significant amount of water is also stored in the Earth's crust, mantle, and core existing primarily in hydrated minerals, most phyllosilicates exemplified by clay minerals. Also, only about one-third of the world's potential fresh water can be used for human needs. As pollution increases, the amount of usable water decreases. Water pollution is due to two main pollutants: chemical (geogenic inorganic both natural and derived from mining practices mainly from tailings and synthetic organic) and pathogenic. Geogenic inorganic pollutants include heavy metals (e.g., Cr, Ni, Cu, Zn, Cd, Pb, Hg, and U) and metalloids (e.g., Se and As). Synthetic organic pollutants include pesticides, biocides, and pharmaceuticals.

Water contributes significantly to health, and good health is the essence of development. However, water's protective role is largely unseen and taken for granted in the wealthier countries. Its contribution to health is directly within households through food and nutrition and indirectly as a means of maintaining a healthy, diverse environment. These two precious resources – water and health – together could enhance prospects for development.

In humans, about 60–65% of the body weight is represented by total body water (TBW), distributed into intracellular and extracellular fluid compartments, which contain about 65% and 35% of total body water, respectively. In the body of a young adult weighing 60–70Kg, there are 40–42 liters of water. In general, men have more 15% of water than women. The water referred to is not pure water; it contains diverse chemical elements in the ionic form (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^-, CO_3H^-, PO_4^{3-}) all essential to life, whose nature and concentration depends upon the cellular function.

The cell membrane regulates the ion exchange between the aforesaid compartments, but water concentration is always maintained. In the extracellular liquid predominates Na^+, Cl^-, and CO_3H^-, whereas in the intracellular liquid predominates K^{1+}, PO_4^{3-}, organic acids, and proteins. Perfect health requires the "dynamic equilibrium" or "hydroelectrolitic equilibrium" between the contents of both intracellular and extracellular compartments. Any rupture of such equilibrium could result from excessive ingestion of food (water included) or excessive water loss and naturally of the minerals in the ionic form it contains due to excessive sweating related to work and heat exposure or to disease (diarrhea or vomits) which could cause dehydration and eventual death.

Water is involved in many bodily functions, since it serves as a carrier of nutrients and substances in the circulatory system. Furthermore, it is the vehicle to excrete products and eliminate waste and toxins, and it also lubricates and provides structural supports to tissues and joints. However, there is no efficient mechanism of body's water storage; therefore, a constant supply of fluids is needed to keep water content.

Natural water can be sweet or fresh and salty. Of all the water that exists in the planet, about 97.5% is salty, that is, it is in the oceans and seas, and its volume is estimated at 1300 million km^3. And, 2% of the water present on Earth is in the form of glacial ice on the north and south poles of the Earth.

It should be noted that the water molecule is the most amazing and abundant molecule in the universe. The water molecule consists of the association of two hydrogen atoms (H) attached to one oxygen atom (O) making the bonds with an angle of 104°. Thus, the water molecule is morphologically symmetric but electrically asymmetric and dipolar: on one side it has a negative electric charge; on the other side it has a positive electric charge. The relatively strong hydrogen bonding between water molecules gives water its relatively high melting and boiling temperatures.

In more detail the water molecule (H_2O) is a complex body resulting from the combination of three isotopes of oxygen (^{16}O, ^{17}O, ^{18}O) and three isotopes of hydrogen (^{1}H, ^{2}H called *deuterium*, and ^{3}H called *tritium*). With regard to oxygen isotopes, the relative abundance is as follows: ^{16}O (99.762%), ^{17}O (0.038%), and ^{18}O (0.200%). With regard to hydrogen's stable isotopes, the relative abundance is as follows: ^{1}H (99.985%) and ^{2}H (0.015%). Isotopes of one chemical element are just distinguished by the number of neutrons existing in the element nucleus.

The so-called isotopic hydrology or isotopic hydrochemistry is of paramount importance to determine the source of the water reservoirs or aquifers, the recharge processes, and the characterization and understanding of the relationships between underground aquifers and surface aquifers.

The stable isotopes ^{18}O and ^{2}H are intrinsic tracers of the water molecule and of the total water cycle that is a characteristic of our planet. These and other achievements are the result of the recent developments on isotopic analysis, as is the case of mass spectrometry with plasma source and multi-collection MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry).

A hydrogen atom (H), the smallest and simplest chemical element, has only one electron which is easily shared by an oxygen atom (O), which is electronegative and seeks to attract electrons. In the presence of hydrogen atoms, each oxygen atom attracts two hydrogen atoms. In the water molecule, the chemical bonds between O and H are covalent, and when several water molecules are present, hydrogen bonds or bridges are formed between the molecules responsible for the expansion when solidification or freezing occurs. Water molecules characterized by constant vibration and interaction bond tightly to one another. When the water freezes, an ordered structure of hexagonal crystals is formed, supported by regular hydrogen bonds.

Given both oxygen and hydrogen in the form of gases in the Earth's atmosphere, it could be assumed to be easy to make water by forced collision between them. But this is not so because the reaction involved is generating a large amount of energy and may even be explosive. Therefore, the alternative to the production of water in this way is the extraction of water already present in the atmosphere in the form of steam through a process called condensation. For this purpose, when using chilled metal blades, the temperature of the surrounding air decreases rapidly, the water vapor condenses, and the water production takes place. The *Whisson windmill* is the material expression of this process. When cooled the blades spin; they can condense up to 12,000 l of water every 24 h. The chemical elements oxygen (O) and hydrogen

(H) are, among all the natural chemical elements, the largest formers of minerals. Water is a constituent of many minerals, particularly silicates that dominate the Earth's crust, and can participate in two chemical forms: H_2O and HO (hydroxyl).

On Earth, water is the only natural substance that can occur in three distinct physical states: liquid, solid, and gas. Switching from one state to another does not involve chemical changes requiring only an increase or decrease in energy, in the form of heat or pressure.

In liquid water the molecules move freely occupying a defined volume, but if cooled the molecules lose kinetic energy and approach a rigid structure called ice (freezing). However, if the liquid water is heated, that is, by adding energy, the movement of the molecules accelerates progressively increasing the free energy until it passes to the state of water vapor or gas (evaporation). This water vapor, if it is cooled, releases energy, which allows the movement of water molecules to slow down until liquid water (condensation) forms.

Water is also present in other asteroids. For example, in the Moon it occurs as ice water at the poles, and on Mars there is information that liquid water has existed in the past. Even comets are true cold-water warehouses, and in the first million years of the Earth, this would have suffered numerous comet impacts, assuming that 30% of the water on Earth has originated in comets.

The Moon, Earth's natural satellite, would have been the result of a massive collision that shortly after the Earth's formation about 4.5 Ga ago would have occurred between a huge unknown star and Earth, a collision that would have provided a start part of the Earth.

A team of specialists in planetary geology at Brown University, in Providence, and the Carnegie Institution, both in the United States, has recently admitted that the portion ripped from the Earth and made into the Moon took with it some of the water that would already exist in the so-called proto-Earth, justifying the fact that the Moon has water inside under the mantle and also at the surface in the form of ice. The team of researchers came to this conclusion after analyzing samples of lunar rocks brought to Earth by the Apollo XV and Apollo XVI missions, and the analyses confirmed the presence of hydrogen and deuterium (the heavier isotope of hydrogen). The obtained measurements are consistent with the measurements obtained in meteorites of the chondrocyte type, whose water has the same geochemical signature of the water present on Earth. The water then in the proto-Earth would have been transferred to the Moon after surviving the vaporization produced by the gigantic impact referred to above. If so, the impacts of chondrite type meteorites (stony meteorite containing small round and glassy granules called chondrules) as well as the aforementioned impacts of comets will be a common source of Earth and Moon water.

It is interesting to note that there are researchers who admit the existence of an immense reservoir of water in the deep interior of the Earth, in the zone of transition of the upper mantle to the lower mantle, between 410 and 660 km of depth. This hypothesis was very recently supported on investigation whose results are reported in the scientific journal *Nature* dated of March 2014, regarding the discovery in Brazil of *ringwoodite*, mineral (previously only identified in meteorites rather than Earth) included in a diamond that had been harvested in 2009 in the region of Juína, Mato Grosso.

The mineral *ringwoodite*, a high-pressure polymorph of the mineral named *olivine*, $(Mg,Fe)_2SiO_4$, and containing 1.5% water, would have been brought from the abovementioned depths to the surface associated with a kimberlite by volcanism. If this large reservoir of water present in the interior of the Earth is confirmed, it could have an important influence on marked geological phenomena such as plate tectonics and volcanism and justify a revision of the theories that explain these natural phenomena.

Less than 1% of the water present on Earth is liquid fresh water, potentially available for drinking, irrigation, and industrial use. And, much of this water occurs in aquifers, that is, natural, underground reservoirs.

Water is not only the basis for human existence. Also, it could become a fuel for human mobility. In the European Union, automobiles are responsible for about 30% of CO_2 emission. Motor cars 100% electric, and hybrid solutions, are being worldwide sought, and water can provide an important contribution for the electrification solution. Hydrogen could be the nontoxic, insipid, colorless, and odorless *gas fuel* obtained from water electrolysis. The separation of hydrogen from oxygen in water molecules by electrolysis was demonstrated in 1800 by the British scientists William Nicholson and Anthony Carlisle who have used electrical discharges for that purpose. The first automobile using hydrogen as fuel was built by Toyota in 2014, first commercialized in Japan, the USA, Germany, Denmark, and United Kingdom. New generations of cars using *fuel cell* already are more advanced than the electric cars in terms of autonomy, and in the near future the *hydrogen fuel cell* will see increased its capacity.

The so-called *green* H_2 can be obtained through water electrolysis with separation of H_2 molecules from O_2 molecules using electricity from renewable sources, for example, solar energy. The required water can be fresh, desalted water, or treated wastewater. The production of 1 Kg of *green* H_2 requires approximately 9 l of water and 1 Kg of *green* H_2 having an energy power of 40 KWh. *Green* H_2 can be incorporated up to 15% in natural gas and can also replace the so-called *blue* H_2 obtained from the use of natural gas to perform the water electrolysis. Currently, in terms of mobility of light vehicles, the competitiveness of *green* H_2 in relation to the electrical battery, e.g., the lithium battery, is economically debatable. However, for heavy vehicle mobility, the H_2 will be unsurpassed. *Green* H_2 will be soon used as a clean alternative technology in all transportation vehicles which today use fossil fuels, as well as in all industries actually using fossil fuels where production could not be electrified. There are great expectations about the decisive contribution of *green* H_2 for significant world decarbonation.

In Portugal, in 2030, all the required energy is expected to come from renewal sources – water, wind, and Sun. Also, there is a plan to initiate in 2022 the production of *green* H_2, the source being seawater in the industrial pole of Sines located in the southwest coast of the country. Sines is the main port in the Ibero-Atlantic front being an open deepwater sea port with excellent maritime access and offering unique natural characteristics to receive any type of vessels, where exists a worldwide extent logistic platform able to receive the main players of port, maritime, industrial, and logistic sectors. Unlike the fresh mineral water from surface and underground reservoirs, ocean water is inexhaustible. Expectations are high regarding the decisive contribution of *green* H_2 for the total decarbonation of the Portuguese energy sector. The energy required to perform the water electrolysis would come from solar energy.

The water used by humanity, which depends on it, has three main sources: surface water (rivers and lakes), groundwater, and atmospheric water (rain). About 70% of the water extracted from the environment, both superficial and underground, is used in agriculture, 23% is used in industry, and 7% is used in our homes.

In the natural environment, there is another type of water that is salty, which is called salt water that occurs in the seas and oceans, making up about 97% of the total water of our planet. In many coastal areas, the fresh drinking underground water is progressively getting salty, a situation that inhibits its drinking and crop growth in agriculture. Such is due to marine salt intrusion into groundwater aquifer owing to overexploitation of aquifers and to sea level rise.

The salts existing in the water of seas and oceans come from the dissolution of minerals from rocks, sediments, and soils that exist in the surface layers of the continents, from rocks and sediments that exist at the bottom of the seas and oceans, and from submarine volcanic emissions and atmospheric deposition.

Salt water in relation to fresh water has a lower freezing point, i.e., it freezes at the lowest temperature, has a higher density, has a higher electrical conductivity, and is slightly alkaline or basic (pH between 7.5 and 8.5), and as opposed to which, it is, as a rule, slightly acidic (pH between 5.5 and 6.5).

Almost all water is in the seas and oceans and is not used for human consumption. But the water of seas and oceans is home to three-fourths of all life on Earth. Only about 3% of fresh water exists on Earth but three-fourths of it is permanently icy. Therefore, only 1% of the Earth's water is available for human use, and to be drinkable it must be colorless, odorless, and tasteless.

Pure fresh water has pH = 7, but as a rule, the fresh water that is ingested has a pH lower than 7, and in a smaller number of cases, it may have a pH higher than 7. Human blood has pH within the range 7.35–7.45, a value strictly regulated by organs like lungs and kidneys. The pH scale ranges from 0 (the most acidic term) to 14 (the most basic term). Rainwater, as a rule, has pH between 4.2 and 4.4. Vinegar and lemon juice have pH values close to 2.

Already it is important to mention that the planet Earth is also known by the name blue planet, because of the blue tonality that it exhibits when it is seen from the space. This tonality is not due to water but rather to atmospheric gases, oxygen, nitrogen, and others. On the surface the seawater displays in many places turquoise color, that is the result of the mirror effect that reflected the equally blue color of the sky when clear.

On average, seawater in the world's oceans has salinity estimated at about 3.5% or 35 g/L (grams per liter). But salinity in the confined water masses (e.g., the Dead Sea that really is a salted lake) can be considerably higher, allowing the bodies to float without the need for normal movement in the normal sea. The anions chloride, carbonate, and sulfate and the cations calcium, sodium, magnesium, and potassium are predominant in the water of oceans and seas. The Dead Sea is a Thalassotherapy Natural Resort of excellence, worldwide.

The oceans and seas are genuine mineral factories or breeding sites, with a strong emphasis on the minerals of the carbonate group, among which the mineral *calcite*, $CaCO_3$, is the most dominant. These carbonates by chemical precipitation or by the accumulation of exoskeletons of various marine beings in the bottom of oceans and seas give rise to the so-called carbonated rocks, among them limestone. Another group of minerals also created by the sea deserves prominence. This is the case of chlorides, represented by minerals *halite*, NaCl, and *sylvite*, KCl.

Oceans and seas play a key role in climate and weather conditions on the continents because they dominate the water and carbon cycles, moderating temperature fluctuations and maintaining the stability of the composition of the atmosphere. In fact, the ocean absorbs, stores, and transports heat. The ocean absorbs about half of the carbon dioxide (CO_2) emitted into the atmosphere. The huge masses of ocean water absorb much of the solar radiation that hits the Earth and release heat through evaporation. In the atmosphere the condensation of the water vapor causes clouds and precipitation or rain.

The ocean and man are closely intertwined. The ocean is a source of food, of oxygen, and indirectly of fresh water, since most of the rain is generated in the ocean. The ocean is a habitat of very diverse ecosystems, some that are independent of solar energy and photosynthesis, but whose distribution is not uniform, more abundant in certain places and scarce in others. The ocean also serves as a way to communicate between people and freight. In addition to the positive effects mentioned above, the oceans can also have negative effects, particularly on human life and property, as hurricanes, typhoons, and cyclones whose devastating effects are well known have their origins in the oceans.

In Portugal, only 20% of the available water resources are used, with the agriculture sector consuming 75%, the energy sector 15%, the urban sector 6%, and the industrial sector 4% of the volume of water available, which necessarily means that the efficiency of water use needs to be improved. In fact, a decade ago the waste of water in agriculture was around 40%. But since then water management has become more efficient. At present, water waste has already fallen to less than 37%, and the National Plan for Efficient Water aims to achieve a goal of 35% in 2020. And, the use of new irrigation technologies and better training of farmers contribute to this.

About 4000 km^3 of mineral water is extracted from surface and underground reservoirs around the world to meet the needs of humanity. In relative terms most of the water used in human activities returns to the environment, only a small part being consumed. It is estimated that about 50% of the water extracted for agriculture is not recovered and is consumed. By contrast, most water used for industrial and household purposes is not consumed. For example, almost all the water used in hydroelectric power plants returns to rivers after use without appreciable change in their properties.

In Portugal, *natural mineral waters* are geological resources that belong to the public domain, that is, their exploitation requires a concession issued by the central government. In turn, spring waters are geological resources that belong to the private domain.

As a final note regarding climate change impacts on ecosystems, particularly on water resources and water quality, the temperature of surface water is expected to increase as a result of global warming. Some human-induced climate change can be mitigated but is considered unavoidable. However, water supply and water quality has received insufficient attention by hydrology experts about the potential impacts of climate changes in air temperature and rainfall, the more frequent droughts in the summer as well as flash-flooding (Delpla et al. 2009; Whitehead et al. 2009). Climate change impacts on surface water systems are easier to investigate on regional and local scales than on a global scale. Consequences on chemical and microbiological water quality are expected. In Western Europe metal concentrations in rivers and lakes have decreased in the past decades with industrial and urban wastewater treatment efforts. Droughts may have negative impacts on metal concentration, and any decrease in inorganic and organic colloids responsible for metal complexation and deposition will cause metal and microbial increase in the water. There is an urgent need for water quality monitoring.

The global surface temperature has increased by 0.74 °C during the past 100 years (1906–2005) according to the International Panel on Climate Change (IPCC) following the Bali Conference (Rosenzweig et al. 2007). Global warming is an indisputable fact, and the average rate of warming over the last 50 years (0.13 ± 0.03 °C per decade) is nearly twofold higher than that observed over the last 100 years (Trenberth et al. 2007).

The impact of climate change on water resources physicochemical parameters, micropollutants, and biological parameters has been a matter of concern, on both global and regional and local scales, among scientists and the governments of all countries (Xia et al. 2014). At last, concerns are growing over surface water quality due to widespread microbial contamination of water systems (Islam et al. 2018). Increasing temperature and change in rainfall patterns combined with socioeconomic factors, such as human and animal population growth and land use changes, will continue to affect flows and water quality in river systems globally (Jin et al. 2015).

13.3 Drinking Mineral Water: Typology and Function

13.3.1 Basic Information

The fresh mineral water consumed by man is classified into three fundamental types: *natural mineral water*, *spring water*, and *tap water*. The first two types of mineral water are underground water and are extracted for consumption from deep or shallow reservoirs, unlike the surface water flowing in rivers and streams and the equally sweet or fresh water that exists in lakes, currently used as tap water at our homes.

Natural mineral water is a water of deep or extensive circulation within the terrestrial crust, bacteriologically acceptable, which presents physicochemical properties stable in its emergence. The reference values for the physicochemical parameters of natural mineral water are defined by Directive 2009/54/EC of the European Parliament and of the European Council of June 18.

The physicochemical parameters of spring water, because its underground circulation is less deep and extensive, are a bit more tolerant, and those parameters are yet more tolerant for tap water. In Portugal, the reference values of the physicochemical parameters of spring water are defined in the Decree Law n.º 306/2007 of August 7.

The water circulating through and across the rocks extracts from them by dissolving the constituent chemical elements of minerals in the ionic form, such as sodium, potassium, calcium, magnesium, iron, silicon, aluminum, etc., and the foregoing water properties may provide therapeutic benefits or simply favorable effects. The emergence of this type of water can be natural (*spring water*) or be captured by means of a borehole more or less deep; in the latter case, the designation of *natural mineral water* does not make total sense.

The nature of the predominant anions and cations in *natural mineral water* determines their chemical composition and nomenclature: sulfate, sulfurous, bicarbonate, chlorinate, silicate, brominate, iodinate, and fluorinate, regarding the predominant anion; and sodium, calcium, and magnesium regarding the predominant cation. Mineral quality and quantity are responsible for mineral water particular profiles, including clearness, color, odor, and taste of both natural mineral water and spring water.

In limestone regions, for instance in the central and southern maritime coasts of Portugal, there is natural mineral water and spring water classified as bicarbonate and calcium-magnesium-bearing hard water. It is water that is easily recognized by the fact that soap does not make or foam when used for washing hands, also because pots, pans and stainless steel from dishwashers are stained after use in kitchens and also because of the dishes and glasses after washing in the dishwashers if they show spleen. To counteract the latter effect referred to, and provide brightness to the washed pieces, it is usual to add purified salt (NaCl) at the start of the wash.

There are *hard* and *soft* mineral waters, the hard ones being characterized by high Ca and Mg contents, despite having other dissolved chemical elements/minerals. *Water hardness* parameter has been relatively undervalued from the health point of view, in particular in medical hydrology.

The concept of total dissolved solids (TDS) in drinking water, as is the case of tap water, is different to the concept of total mineralization (TM); the first, TDS, comprises the inorganic solid constituents also called salts plus small amounts of organic and colloidal matter, particularly polar organic compounds which are dissolved in water, and as so they could not be filtrated; the last, TM, exclusively comprises dissolved minerals in the elemental form, as cations and anions.

Whenever drinking water bears extremely finely particulate suspended solids, these should be filtrated before TDS analytical assessment. Suspended solids will not pass through a filter, whereas dissolved solids will. TDS can be determined by evaporating a prefiltered sample to dryness and then finding the mass per liter of the dry residue of the water sample. TDS is sometimes used as a "watchdog" environmental test. Any change in the ionic composition between testing sites in a stream can quickly be detected using a conductivity probe. Further tests can then help to determine the specific ion or ions that contributed to changes in the initial TDS reading. However, in natural mineral waters due to their deep source and circulation, the organic component content is almost nonexistent, the reason why TDS and TM values corresponding to a certain natural mineral water are coincident or almost coincident. Total mineralization of natural mineral water can change along the hydrological year, and the control of the resulting periodic changes can be done measuring the *specific electric conductivity* (μS/cm), an important water parameter when natural mineral water is used in health resort medicine.

The parameter dry residue (DR) is also used in drinking water characterization, and it is assessed by evaporation of 1 L of water at 180 °C.

TDS, TM, and DR values in waters bearing or originating volatiles when heated up, for instance in the case of bicarbonate waters, are always lower than they theoretically should be, because in the case of bicarbonate waters, bicarbonate HCO_3 decomposes into H_2CO_3 and CO_2, and this being a gas gets evolved.

In the USA bottled water must contain at least 250mg TDS to be labeled as mineral water.

HCO_3 in water is formed by the reaction of CO_2 dissolved in water with Ca- and Mg- bearing carbonate minerals present in soils and rocks. HCO_3 inside the human body is formed from the reaction of CO_2 produced from carbohydrate metabolism with OH from water: $CO_2 + OH \longleftrightarrow HCO_3$, and this HCO_3 being absorbed by the body fluids contributes for their pH increase.

Regarding drinking water mineralization, the European Union legislation proposes the following classification: *very low mineralized* or *hyposaline*, up to 50mgL^{-1}; *low mineralized*, 50–500 mgL^{-1}; *mineralized*, 500–1500 mgL^{-1}; and *highly mineralized* or *hypersaline*, >1500 mgL^{-1}. This classification is currently extended to natural mineral waters used in health thermal resorts where health resort medicine is practiced.

The classification of Krieger (1963) is currently used to classify drinking water into five groups based on TDS: fresh or very low mineralized waters (TDS 0–1000 ppm), slightly saline waters (TDS 1000–3000 ppm), moderately saline waters (TDS 3000–9000 ppm), highly saline waters (TDS 10,000–35,000 ppm), and brine waters (TDS >35,000 ppm).

Based on dry residue (DR) values, mineral waters are classified as follows: fresh water, <2000 mgL^{-1}; brackish water, 2000–5000 mgL^{-1}; salt water, 5000–40,000 mgL^{-1}; and brine water, >40,000 mgL^{-1} (Custódio and LLamas 1996).

In mainland Portugal the fact that about 2/3 of the territory is occupied by granite rocks and similar rocks justifies the figure of about 80% of hypomineralized natural mineral water and spring water.

The estimation of total dissolved solids (TDS) or total dissolved minerals in water could be easily and cheaply assessed measuring the water electric conductivity expressed in millisiemens per meter (mS/m) or millisiemens per centimeter (mS/cm).

Distilled water conductivity is <1μS/cm, rainwater conductivity in clean areas is <1–5μS/cm, hyposaline mineral water conductivity is 30–100μS/cm, hypersaline mineral water conductivity is 250–600μS/cm, and seawater (salinity 3–3.5%) conductivity is 40,000–50,000μS/cm.

13.3.2 Physical, Chemical, Physicochemical, and Microbiological Properties of Water for Human Consumption

It is not only *natural mineral water* that is good for human health. Other groundwater and even surface water are equally good for health and indispensable for human consumption. In the twenty-first century, humanity is facing many problems related to water quantity and/or water quality (UNESCO 2009). And these problems will be aggravated in the future due to climate changes resulting in higher water temperatures, melting of glaciers, more floods and droughts (Huntington 2006; Oki and Kanae 2006).

Regarding human health the most direct impact is the lack of adequate sanitation of safe drinking water. Additional threats include the exposure to pathogens (Fenwick 2006) and to chemical toxicants. Presently drinking water security is a global concern, and still millions of people lack daily access to clean and safe drinking water. What matters is that the water that man drinks and uses for cooking (cleaning and cooking) and for his hygiene must be drinkable, and such accomplishment requires the following properties:

> *Clearness, colorless, odorless, aerated, cooking food well, free of organic matter and substances toxic to the organism, and also free of pathogenic germs capable of causing the onset of diseases.*

In Portugal, for this purpose, the water must be treated from the physicochemical point of view, and according to the Water and Waste Services Regulatory Body (ERSAR), water must comply with the requirements set out in Table 13.1.

Other chemicals should be taken into account. For example, *fluoride* concentrations to be beneficial should be between 0.8 and 1.0 mg/L, because if they are higher than 1.0–1.5 mg/L they can cause *dental fluorosis* and *skeletal fluorosis*. Also nitrate concentrations exceeding 45 mg/L can cause health problems, particularly in children.

Aluminum (Al) is a natural constituent of many rock-forming minerals, being the most abundant metal in the Earth's crust. Also, Al is extensively found in clays, as a rule hydrous aluminum silicates and weathering products of the rock-forming minerals. Aluminum is naturally found in drinking water in the form of very fine

Table 13.1 Factors and substances that influence water potability

Substances	Maximum acceptable	Maximum admissible
Total solids	500 mg/L	1500 mg/L
Color	5 units (Pt-co)	50 units
Turbidity	5 units (UT)	50 units
Taste	Subjective limit	Subjective limit
Smell	Subjective limit	Subjective limit
Iron (Fe)	0.3 mg/L	1 mg/L
Manganese (Mn)	0.1 mg/L	0.5 mg/L
Copper (Cu)	1.0 mg/L	1.5 mg/L
Zinc (Zn)	5.0 mg/L	7.5 mg/L
Calcium (Ca)	75 mg/L	200 mg/L
Magnesium (Mg)	50 mg/L	150 mg/L
Sulfates (SO_4)	200 mg/L	400 mg/L
Chlorides (Cl)	200 mg/L	600 mg/L

clay particles suspended in the water. Aluminum is also used to improve water quality in plants doing drinking water treatment, and in some of those plants incomplete removal of Al can result in elevated Al concentrations in treated water.

Still other substances of which the following minerals are examples may also have influence on the potability of water.

Arsenic (As) also can be a contaminant of drinking water; its source includes natural weathering of minerals such as arsenopyrite (FeAsS) and pyrite (FeS_2). Arsenic's relatively high concentrations can be found in certain groundwater reservoirs. Consumption of water containing As concentrations above drinking water guidelines over long periods of time can cause a variety of health effects. The trivalent form As(III) is the most toxic, followed by the pentavalent form As(V), and then by the organic forms. The average person consumes about 10μg/day of As through water and food (particularly seafood and meat); however, As in food is usually found in the less toxic organic forms (*In*: Ritter et al. 2002).

Iron (Fe) and Manganese (Mn) are very common in drinking water, and their concentrations do not present any significant hazards to human health, but modifying the aesthetic water quality guidelines (300 and 50μg/L for Fe and Mn, respectively) is set to prevent undesirable taste and color.

These and other metals and metalloids such as lead (Pb), cadmium (Cd), mercury (Hg), selenium (Se), uranium (U), zinc (zn), and chromium (Cr) in drinking water and corresponding health effects are reported (Health Canada 1997; Ritter et al. 2002).

Guidelines on maximum recommended levels for a range of chemicals/minerals dissolved into drinking water have been developed. The maximum permissible concentrations expressed in mg/L are as follows: lead (Pb), 0.05; arsenic (As), 0.05; selenium (Se), 0.01; chromium (expressed as hexavalent Cr), 0.05; cadmium (Cd), 0.01; and barium (Ba), 2.00. For instance, *arsenic* toxicity in drinking water has been classified by the WHO as a world public health concern, in countries like Bangladesh where million people consume water from As contaminated water wells.

So far, the harmful effects of elements/minerals in drinking water are less investigated and known than the beneficial effects. Hopefully the investigation on both negative and positive effects should be carried out at the same extent. There may still be substances of an organic nature that influence the potability of water.

The treatment of water, particularly of surface reservoirs in order to make it drinkable, usually involves two operations:

1. Filtration (removal of substances in suspension by the passage of water through a filter bed of more or less fine sand)
2. Disinfection (elimination of pathogenic microorganisms by the use of chlorine (potent antiseptic, in the liquid or gaseous state)

Other operations may still take place, such as the following:

3. Coagulation-flocculation – combining the use of chemicals, for example, aluminum sulfate, to cause aggregation of colloidal particles of organic matter and clay minerals to remove color and turbidity
4. Fluoridation – to prevent tooth decay by adding fluoride in water
5. Softening – to decrease water hardness
6. Correction of aggressiveness – to correct the acidity of the water, expressed by acid pH, that is, significantly less than 7, in the sense of approaching this value

Table 13.2 shows the requirements, i.e., the guideline values and parametric values expressed in mg/L which, in 2011, by both the WHO (World Health Organization) and the EU (European Union), respectively established for water with respect to the minerals in solution. As a rule, concentrations of the so-called macrominerals or macroelements (e.g., calcium, magnesium, bicarbonate, and sulfate) are expressed in mg/L, while concentrations of the so-called microminerals or microelements (e.g., selenium, lithium, boron, and molybdenum) are expressed in µg/L.

Table 13.3 shows the range of concentrations (in mg/L) recommended for macroelements/macrominerals present in drinking water. The desirable range of pH is 7.0–8.0.

Minerals in drinking water are classified into two groups: *macrominerals* and *microminerals*, both essential to good health, naturally if they do not occur in excessive or deficient concentrations relatively to the reference concentrations.

A rather significant amount of information about the health effects of the most important macrominerals (HCO_3 or bicarbonate, SO_4 or sulfate, Cl or chloride, Ca, Mg, K, and Na) and microminerals (Fe, I, F, Mn, Li, B, Si, Cr, Se, Cu, Zn, Mo, and V) present in drinking water is currently available.

With regard to macrominerals, Rosborg and Kozisek (2015a, b) report their optimum concentrations for better protecting against diseases, as well as their functions, benefits, and risks. And, with regard to microminerals, Rosborg et al. (2015a, b) report their optimum concentrations for better protecting against diseases, as well as their functions, benefits, and risks.

Table 13.2 Guideline values and parametric values established by the WHO (2011a) and the EU (2011) for maximum concentrations of minerals present in solution in drinking water (*In*: Rosborg and Kozisek 2015a, b)

Parameters/minerals	Symbols	Guideline values, WHO	Parametric values, EU
pH	pH		6.5–9.5
Antimony	Sb	0.02 mg/L	0.005 mg/L
Aluminum	Al	0.9	0.2
Ammonium	NH_4	n.e.	0.50
Arsenic	As	0.01 (A.T)	0.01
Boron	B	2.4	1.0
Barium	Ba	0.7	n.e.
Beryllium	Be	0.012 n.e.	n.e.
Bromate	BrO_3	0.01 (A.T)	0.01
Cadmium	Cd	0.003	0.005
Cyanide	CN	0.5 n.e.	0.05
Lead	Pb	0.01 (A.T)	0.01
Chloride	Cl	250	250
Copper	Cu	2	2.0
Chromium	Cr	0.05 (P, total Cr)	0.05
Iron	Fe	2	0.2
Fluoride	F	1.5	1.5
Manganese	Mn	0.4 n.e.	0.05
Mercury	Hg	0.006	0.001
Molybdenum	Mo	0.07 n.e.	n.e.
Nickel	Ni	0.07	0.02
Nitrate	NO_3	50	50
Nitrite	NO_2	3	0.5
Selenium	Se	0.04 (P)	0.01
Sodium	Na	200	200
Sulfate	SO_4	500	250
Uranium	U	0.030 (P)	n.e.
Zinc	Zn	3	n.e.
Radioactivity		10 Bq/L, 0.1 mSv/year	0.10 mSv/year

Note: *n.e.* value not estimate or assessed, *A* provisional value, *T* provisional value, *P* provisional value

Table 13.3 shows the range of concentrations (in mg/L) recommended for macroelements/macrominerals present in drinking water, from the health point of view (Rosborg and Kozisek 2015a, b, *In*: Chapter 3 of "Drinking Water Minerals and Mineral Balance," Rosborg I (editor), Springer).

Also, Table 13.4 contains the suggested desirable ranges for some microelements/microminerals present in drinking water from the health point of view (Rosborg, Ferrante and Soni 2015, *In*: Chapter 4 "Drinking Water Minerals and Mineral Balance," Rosborg I (editor), Springer).

Table 13.3 Recommended concentration ranges of main *macrominerals* present in drinking water (Rosborg and Kozisek 2015a, b)

Parameters	Concentration range in mgL^{-1}
Calcium	20–80
Magnesium	10–50
Bicarbonate	100–300
Sulfate	20–250
Fluoride	0.8–1.2
TSD (total solids dissolved)	100–500

Table 13.4 Suggested desirable concentration ranges for some microelements in drinking water from the health point of view (Rosborg et al. 2015a)

Parameters	Concentration in mgL^{-1}
Boron (B)	0.1–1
Chloride (Cl)	20–100
Chromium (Cr)	0.01–0.05
Cobalt (Co)	0.005–0.02
Copper (Cu)	0.02–02
Fluoride (F)	0.8–1.2
Iodine (I)	0.005–0.075
Iron (Fe)	0.02–0.2
Lithium (Li)	0.05–0.2
Manganese (Mn)	0.02–0.05
Molybdenum (Mo)	0.005–0.02
Phosphate (PO_4)	0.02–0.1
Rubidium (Rb)	0.1–1
Selenium (Se)	0.005–0.05
Silicon (Si)	2–10
Vanadium (V)	0.001–0.01
Zinc (Zn)	0.02–0.2

Yet also the Table 13.5 shows the suggested safe concentration upper limits for some potentially toxic macrominerals and ions in drinking water from the health point of view (Rosborg, Soni and Kozisek 2015, *In*: Chapter 5 of "Drinking Water Minerals and Mineral Balance," Rosborg I (editor), Springer.

The book entitled *Drinking Water, Minerals and Mineral Balance: Importance, Health Significance, Safety Precautions* (editor Rosborg I 2015) presents the current knowledge of the beneficial and deleterious effects of both *macrominerals* and *microminerals* present in solution in drinking water in the health of man and other animals. Two other books dealing with drinking water should be emphasized, one entitled *Geography and Health: A Nordic Outlook* by Schaerström et al. (2014) and the other entitled *Calcium and Magnesium in Ground Water: Occurrence and Significance for Human Health* by Razowska-Jaworek (2014).

Table 13.5 Suggested safe concentration upper limits for some potentially toxic macrominerals and ions in drinking water from the health point of view (Rosborg et al. 2015b)

Parameters	Concentration in mgL^{-1}
Aluminum (Al)	<0.2
Ammonium (NH_4)	<0.5
Antimony (Sb)	<0.005
Arsenic (As)	<0.01 (0.001–0.01)
Barium (Ba)	<0.7 (0.07–0.7)
Beryllium (Be)	<0.005
Bromate (BrO_3)	<0.01
Cadmium (Cd)	<0.003
Cyanide (CN)	<0.1
Lead (Pb)	<0.01
Mercury (Hg)	<0.001
Nickel (Ni)	<0.05 (0.01–0.05)
Nitrate (NO_3)	<50
Nitrite (NO_2)	<0.5
Radioactivity	<10 Bq/L, <0.1 mSv/year
Silver (Ag)	<0.01 (0.002–0.01)
Strontium (Sr)	<0.02–0.2
Tin (Sn)	<0.1 (0.01–0.1)
Titanium (Ti)	Not set
Uranium (U)	<0.015

The function of *macrominerals* existing in drinking water (natural mineral water and spring water), and the health disorders their excess or deficiency may cause are herewith presented based on a considerable amount of currently available information; naturally the body minerals content and balance depends not only of drinking water, it also has source in dietary solid food (Burckhardt 2008; Rosborg and Kozisek 2015a, b).

Calcium (Ca^{2+}) – It is a major and vital mineral present in the generality of drinking waters. It is derived from the dissolution of Ca-bearing rock-forming minerals, such as calcite, dolomite, gypsum, calcic-sodic feldspars, pyroxenes, and amphiboles. A lifelong regular daily Ca intake is important to maintain Ca balance and healthy bone and teeth. Ca is indispensable for multiple enzymatic functions, such as cardiovascular activity, blood coagulation, and nervous system activity. Ca excess can cause coronary and vascular cerebral diseases and renal lithiasis. Ca deficiency can cause osteoporosis (Aptel et al. 1999; Bacciottini et al. 2004; Bohmer et al. 2000; EFSA 2016; Kozisek 2003; Kozisek et al. 2015; Meunier et al. 2005; Rosborg 2015; Roux et al. 2004).

Magnesium (Mg^{2+}) – It is frequent in natural mineral waters generally associated with calcium, although in relatively lower concentrations. It is derived from dissolution of Mg-bearing rock-forming minerals, magnesite, dolomite, chlorite, olivine, pyroxenes, and amphiboles. Mg is essential for a healthy life, its deficiency being responsible for muscle weakness, cramps, cardiac arrhythmia, and intestinal disorders. Mg induces the stimulation of multiple enzymatic systems and has some influence on the immune system. Mg as $MgSO_4$ can cause nausea, vomiting, and intestinal hyperactivity causing abdominal pain and diarrhea. The current RDI (recommended daily intake) for Mg is about 280–350 mg (NSFA 2012), and a higher RDI value of 450–500 mg is suggested for prevention of coronary heart disease (Altura and Altura 2009; Jiang et al. 2016).

Several studies show the association between high and low Ca and Mg contents of drinking water and human health effects (see Rosborg and Kozisek 2015a, b). Ca and Mg may act as metabolic antagonists. Kousa et al. (2006) based on a study of the diet of Finish rural population showed that high Ca and low Mg contents in drinking water significantly increases the risk of acute myocardial infarction (AMI). Durlach et al. (1989) recommend a Ca/Mg total intake ratio of 2:1.

Sodium (Na^+) – It is also a major and vital mineral in the generality of drinking water. It is derived from Na-bearing rock-forming minerals. Drinking water contains, in general, less than 20 mg/L of Na. However, for instance, in coastal areas Na content can exceed 250 mg/L due to saline intrusion and may cause high blood pressure. Na is essential for body fluid equilibrium. As aforesaid Na concentration is higher in the extracellular fluid relatively to intracellular fluid. The average of 3.3 g/day and the minimum of 500 mg/day are regarded as Na intakes for a healthy life (WHO 2011a, b). Excess of Na in extracellular fluid can cause high blood pressure, while Na deficiency may cause symptoms of nausea, vomiting, convulsion, lassitude, and muscle cramps (Bowman and Russell 2006).

Potassium (K^+) – It is common in all natural mineral waters, although in very low concentrations, as a rule within the limits 0.1–10 mg/L (Aastrup et al. 1995). It is derived from the dissolution of K-bearing rock-forming minerals, such as alkaline feldspars (microcline and orthoclase) and micas (muscovite and biotite). K together with Na is involved in maintaining the body's water balance essential in the ion exchange through cell walls, known as sodium/potassium bomb, responsible for the equilibrium of cellular osmotic pressure. About 95% of the body's K is intracellular. The recommended daily intake of K for adults is 2–4 g/day. Both excess and deficiency of K can lead to disorders in cardiac, muscle, and neurological functions (Anderson et al. 2010). Risk reducing K range has been estimated within 5–10 mg/L, and the desired Na/K ratio is 2–5:1.

Bicarbonate (HCO_3^-) – It is one of the pH regulators in the human body fluids, the carbonic acid/bicarbonate system. Generally drinking water contains 20–400 mg/L HCO_3 (Aastrup et al. 1995; Schoppen et al. 2004), and in non-carbonated water, HCO_3 concentration depends on the Ph. The highest concentration occurs at pH = 7–8 (Rosborg et al. 2003). Carbon dioxide (CO_2) is formed during carbohydrate metabolism, and its reacting with water OH produces HCO_3^- ions which are absorbed in the body fluids and contribute to pH level increase. Bicarbonate waters have this alkalinizing and antacid property; to HCO_3 is attributed the neutralization of stomach acidosis (Petraccia et al. 2006; Jones and Walter 2007). Consumption of bicarbonate water might produce significant reduction in total cholesterol (Pérez-Granados et al. 2010), and as so bicarbonate mineral water could be used in diets to reduce cardiovascular risk and prevent osteoporosis (Wynn et al. 2009a, b). Risk reducing HCO_3 range appears to be 100–300 mg/L (Rosborg and Kozisek 2015a, b).

Sulfate (SO_4^{2-}) – Sulfur participates in the synthesis of many compounds, including *chondroitin* in cartilage, bone, tendons, and blood vessels. Sulfur in natural mineral waters is associated with O in the oxidized form SO_4^{2-} or is associated with H in reduced forms HS^- e H_2S. Drinking water may contain sulfate within the range 10–500 mg/L, but higher concentrations have been reported (Aastrup et al. 1995). Sulfate in drinking water may cause peristaltism and motility in the digestive tract and the increase of secretions of the respiratory system. The reduced forms, particularly the HS^- form, are quickly absorbed both by the internal mucous membranes and by the skin. Sulfur participates in the composition of hormones, as is the case of insulin. Sulfur's reduced forms are found in sulfurous waters (Dawson et al. 2015).

On the other hand, there are *microminerals*, such as Fe, F, As, Se, Zn, Mo, Cr, Cl, P, I, etc., that at optimum low concentrations play important roles on the protection against diseases. However, like in *macrominerals*, their excess or deficiency can cause health disorders (Rosborg et al. 2015a, b).

According to the European Legislation (2009/54/EC Directive), both physical and chemical characterizations are used to make a classification of the different mineral waters, based on the analysis of main parameters (Petraccia et al. 2006).

First of all, *natural mineral waters* are classified on the basis of total dissolved solids (TDS) determined after evaporation of 1 L of water at 180 °C and expressed in mg/L. Table 13.6 shows a current TDS classification based on mineral content. By law there are no upper or lower limits for mineral content in natural mineral water; instead these limits are strictly regulated for drinking tap waters.

Total dissolved solids (TDS) is the term used to describe the total of inorganic salts and small amounts of organic matter present in solution into water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, hydrogen carbonate, chloride, sulfate, and nitrate anions (WHO/SDE/WSH/0.3.0.4/16 2003, background document for the development of WHO Guidelines for drinking water quality). Also the presence of dissolved solids in drinking water may affect water's organoleptic properties, one being the palatability that has been rated by panels of tasters in relation to its TDS level as follows: excellent, less than 300 mg/L; good, between 300 and 600 mg/L; fair, between 600 and 900 mg/L; poor, between 900 and 1200 mg/L; and unacceptable, greater than

Table 13.6 Classification of natural mineral water based on TDS

TDS or residue at 180 °C	Definition
<50 mg/L	Very low mineral content
50–500 mg/L	Low mineral content
500–1500 mg/L	Medium mineral content
>1500 mg/L	High mineral content

1200 mg/L. Water with extremely low concentrations of TDS may also be unacceptable because of its flat, insipid taste.

The method of determining TDS in drinking water supplies most commonly used is the measurement of specific conductivity with a conductivity probe that detects the presence of ions in water. Conductivity measurements are converted into TDS values by means of a factor that changes with the type of water. The practical quantitation limit for TDS in water by this method is 10 mg/L. High TDS concentrations can also be measured gravimetrically, although volatile organic compounds are lost by this method. The constituents of TDS can also be measured individually. As far as being known, health effects associated with the ingestion of TDS in drinking water appear to exist. However, associations between various health effects and hardness, rather than TDS content, have been investigated in many studies. In early studies, inverse relationships were reported between TDS concentrations in drinking water and the incidence of cancer, coronary heart disease, arteriosclerotic heart disease, and cardiovascular disease. Also, total mortality rates were reported to be inversely correlated with TDS levels in drinking water (WHO/SDE/WSH/03.04/16 2003).

Mineral waters are also classified by other physical parameters, such as pH, temperature, hardness, alkalinity, chemical parameters, molecular concentration/osmotic pressure, and radioactivity.

With regard to pH, mineral waters are classified as *acid waters* ($pH < 7.0$), *alkaline waters* ($pH > 7.0$), and *neutral waters* ($pH = 7.0$).

With regard to water hardness, this property indicates the presence of alkaline earth metals (Ca and Mg). The hardness of mineral waters, expressed in mg$CaCO_3$/L or ppm$CaCO_3$/L, may be classified as *very soft* (0–100 mg/L of $CaCO_3$), soft (100–200 mg/L of $CaCO_3$), *hard* (200–300 mg/L of $CaCO_3$), or *very hard* (>300 mg/L of $CaCO_3$) (Albertini et al. 2007). The so-called total hardness (TH) of a mineral water is defined as the sum of the concentrations of Ca, Mg, and other multivalent cations.

Actually, in Canada, drinking water hardness is classified as *soft*, <60ppm$CaCO_3$/L; *moderately hard*, 120–60ppm$CaCO_3$/L; and *hard* >120ppm$CaCO_3$/L.

Water hardness is often expressed in °dH or "Germany degrees," where 1°dH corresponds to 10 mg/L $CaCO_3$, and water hardness classification could be as follows: very soft, 0–2°dH; soft, 2–5°dH; moderately hard, 5–10°dH; hard, 10–20°dH; and very hard, >20°dH.

Water softening filters using ion exchange resins can replace Ca and Mg ions by Na and K ions.

Mineral water alkalinity relates to the presence of bicarbonates and carbonates and other pH reactive species and, like hardness, is expressed in mg$CaCO_3$/L.

Elpiner (1995) reports the increase of *urolithiasis* frequency when groundwater with hardness higher than 10 meqL^{-1} and 300–500 mgL^{-1} of Ca is consumed. Also, several authors, such as Ortiz et al. (1990) and Yang et al. (1996) showed evidence of a correlation between coronary disease and the consumption of soft water, in particular, Mg deficient. In all the cases referred to, the authors do not explain the mechanisms of those interactions.

According to Sauvant-Rochart and Pepin (2002), a link between cardiovascular disease (CVD) mortality and the hardness of drinking water (DW) has been suggested by about 30 epidemiological studies performed worldwide in the general population since 1957. The authors make a review that examines the main ecological studies, case-control studies, and cohort studies, published between 1960 and 2000.

Very soft and acidic drinking water can be remineralized using various processes:

1. Limestone dissolution by carbon dioxide
2. Application of sodium bicarbonate, sodium sulfate, and calcium sulfate
3. Application of hydrated lime and sodium carbonate
4. Application online of micronized lime
5. Application of carbon dioxide and excess of hydrated lime (Brenner et al. 2015)

Also, very hard and alkaline drinking water can be softened using various processes:

1. Addition of lime or sodium hydroxide in order to precipitate Ca salts
2. Ion exchange resins, the Na or K ions that replace Ca and Mg ions, are released into the water
3. Ion exchange filters, using sodium chloride, the Ca and Mg ions being exchanged for Na ion (Rosborg et al. 2006)

Any of the applied treatment processes should preserve or improve as much as possible the drinking water mineral content/mineral balance (Brenner et al. 2015).

Mineral waters are also classified by chemical parameters and are named firstly by the prevalent anion and secondly by the prevalent cation.

The 2009/54/EC Directive classifies mineral waters into the following major classes:

Bicarbonate water, if bicarbonate content (CO_3H^-) is >600 mg/L; *sulfate water*, if sulfate (SO_4^{2-}) content is >200 mg/L; *chloride water*, if chloride (Cl^-) content is >200 mg/L; *fluoride water*, if fluoride (F^-) content is >1 mg/L (more than 1,5 mg/L of fluoride is unsuitable for children below the age of 7); *calcium water*, if calcium (Ca^{2+}) content is >150 mg/L; *magnesium water*, if magnesium (Mg^{2+}) content is >50 mg/L; and *sodium water*, if sodium (Na^+) content is >200 mg/L.

The significant number of clinical studies being carried out so far have provided much information on the mineral medicinal properties of specific natural mineral waters, and about this subject, the article of Quattrini et al. (2016) is an interesting review, and in a very synthetic way, the following notes are below reproduced:

Bicarbonate or bicarbonated mineral waters can provide positive effects on the digestive tract. Studies on crenotherapy treatments and on patients with functional dyspepsia show that the consumption of bicarbonate mineral water may neutralize acid secretion, increase the pH level in the gastric lumen, accelerate gastric emptying, and stimulate the release of digestive hormones, known to have pivotal roles in the regulation of gastric function (Capurso et al. 1999; Bertoni et al. 2002).

Sulfate or sulfated mineral waters are characterized by the presence of sulfate anion associated with cations such as Ca, Mg, and Na, and these cations could provide and enhance water specific properties: magnesium sulfate and sodium sulfate mineral waters demonstrated to be really efficient for functional constipation conditions (Dupont et al. 2014). Drinking mineral water rich in magnesium sulfate and sodium sulfate can confer significant benefits for healthy digestion, in terms of improvement of constipation symptoms, overall bowel movements, and stool consistency (Bothe et al. 2015). Sulfate waters, those that contain sulfate ion (SO_4^{2-}), are balneotherapeutically used mainly in the management of gastrohepatological and biliary conditions in the form of balneological drinking cures or hydropinic therapies (Fraioli et al. 2010; Mennuni et al. 2014; Bothe et al. 2015).

In mineral waters sulfur can occur too as sulfate ion SO_4^{2-} or as hydrogen sulfide gas (H_2S). Drinking of H_2S waters is not common, particularly due to their unpleasant taste and smell, the “rotten egg” smell.

Hydrogen sulfide (H_2S) waters, also called “sulfur waters” and sulfurous waters, are applied mostly in the form of baths defined as H_2S or sulfur balneotherapy and indicated most frequently in the management of rheumatic diseases (Karagülle et al. 1996; Ekmekcioglu et al. 2002; Leibetseder et al. 2004) and a lesser extent in dermatological conditions (Costantino et al. 2005; Huang et al. 2018; Carbajo et al. 2018).

Balneological waters classified as sulfate waters are defined as those containing at least 1200 mg/L sulfate (SO_4^{2-}); the ones originally and naturally containing dissolved H_2S gas with an S^{2-} level at least 1 mg/L are named “sulfur waters” (Karagülle and Dönmez 2002; Karagülle and Karagülle 2019).

Karagülle and Karagülle (2019) report a systematic review aimed to evaluate in vivo experimental studies investigating the biological effects of natural H_2S water drinking in healthy and ill model laboratory animals. The studies have indicated several health effects in mice. The authors question if the in vivo-obtained benefits of biological parameters would exert similar effects on humans undergoing traditional hydroponic therapies or drinking cures with H_2S waters at natural sulfur water spas/health resorts or natural (even artificial) H_2S water consumption at home and conclude that the question would be clarified by clinical trials.

Chloride or chlorinated mineral waters are composed by chloride as predominant element and the most abundant cations are sodium, calcium, and magnesium. Although studies about their health effects are scarce, chloride mineral water may exert their properties for bowel functions: they may stimulate intestinal peristalsis and intestinal secretion of water and electrolytes (Petraccia et al. 2006). Moreover, they may have a choleretic and cholagogue action by increasing biliary secretion and bile inflow into the duodenum (Casado et al. 2015).

Fluoride or fluoridated mineral waters are indicated for children, because they can reduce the incidence of decay and promote bone mineralization. However, high fluoride consumption may have some toxic effects, from dental fluorosis to skeletal fluorosis, if fluoride intake is above 10 mg/L. For this reason, the European Food Safety Agency (EFSA) established fluoride upper limit of exposure to 1.5 mg/L/day (EFSA 2005), a limit that was also confirmed by the World Health Organization (WHO 2011a, b).

It is well established and recognized that minerals are more easily absorbed in the gut if they come from water than from food. Several interesting topics are covered in the book. One of them is the possibility of negative interaction between certain minerals present in the water, as is the case of the antagonistic Ca/Mg interaction. When Ca, essential mineral for the formation of healthy bones and teeth, is in excess in water, this may counteract the incorporation of Mg, essential for a healthy heart. Therefore, an optimum balance between the two minerals present in drinking water is fundamental. The ideal Ca/Mg ratio lies in the range 2–3:1.

The concentration levels of chemical constituents (macroelements as well as microelements, toxic elements included) of certain water, that is, its hydrogeochemical signature, determines water potability and its use in agriculture, recreation, and health and the interactions with biological systems (Zhu and Schwartz 2011).

The negative correlation between the chemistry of drinking water supplies in a certain area and the incidence of cardiovascular disease among the people living in that area has been reported (Crawford et al. 1997; Comstock 1979; Bernardi et al. 1995). Although not being a proven causation, the impact of the inorganic chemistry of the groundwater on cardiovascular diseases has puzzled many researchers (Dissanayake and Chandrajith 2006). Various scientific studies show that hard water bearing high concentrations of Ca, Mg, HCO_3, and SO_4 is protective against cardiovascular diseases. Such correlation has been observed in many countries and in many regions or areas (Dissanayake and Chandrajith 1999), and it has been suggested the Mg present in abundance in the hard water may well be the factor showing cardioprotective influence (Marier 1968; Anderson 1972; Altura and Altura 1991; Rubenowitz et al. 2000).

In Canada, from a survey of 15 elements in 575 drinking water, Neri et al. (1975, 1977) have concluded that Mg is the most likely element that is responsible for the protective cardiovascular effect. The authors based such conclusion on the following facts:

1. Mg was present in more than 10% of the sample waters.
2. Mg is a consistent function of the softness-hardness gradient.
3. Mg represents a significantly high proportion of the daily intake from other sources.
4. The known metabolic effects of Mg are consistent with the hardness-mortality trend.

Since the crustal concentration of Mg is much lower than that of Ca, Mg is found in lower concentrations in natural waters with an average Ca/Mg ratio of 4. According to Kozisek (2003), Mg deficiency is known to be linked to vasoconstrictions, hypertension, cardiac arrhythmia, and acute myocardial infarction, among other

Table 13.7 Suggested concentration ranges for some mineral ratios in drinking water from the health point of view (*In*: Rosborg and Kozisek 2015a, b)

Mineral ratios	Safe conc. range	
Ca/Mg	2–3:1	
Na/Mg	3–4:1	Na < 100 mg/L
Na/Ca	1–3:1	Na < 100 mg/L
Na/K	2–5:1	Na < 100 mg/L
$(Mg + SO_4)$	100–400	Mg < 150 mg/L
$(Ca + Mg + Na + K) = (SO_4 + CO_3 + HCO_3 + Cl)$	Ion balance	Meq/L

cardiovascular diseases. Marier (1978) reported from an analysis of 350 tissue samples from 161 autopsy cases observed that myocardial Mg was 6% lower in "cardiac death" patients from soft water localities in comparison with hard water regions.

The ion balance is an important factor used to check water chemical analytical data. The sum of the anion concentrations should be equal to the sum of cation concentrations.

Table 13.7 shows the desirable concentration ranges for some mineral ratios in drinking water from the health point of view.

In Portugal each citizen spends, on average, 168 liters of water per day. In the country, 926,923m^3/year (34% from boreholes and 66% from dams) are collected, and of the 823,291m^3 of treated water, 693,074m^3 are distributed by consumers, 594,393m^3 for domestic consumption, and the remainder for other uses.

Man has also used water for drinking and for agricultural and industrial purposes, since the earliest civilizations, for hygienic and sanitary purposes. The last two applications referred to degrade the quality of effluent water that is fed into rivers, lakes, seas, and oceans. The microbiological quality of drinking water is inherently linked to sanitary practices, with fecal pathogenic microorganisms being the most common source of contamination.

The filtration of water by the soil and sediments of the aquifers, more efficient when the soils and sediments contain a significant amount of clay (whose micrometric dimension and electric charge favor the fixation of inorganic and organic contaminants), can provide natural protection against the said microorganisms, which is why water from underground aquifers is the most attractive option for the safe consumption of drinking water.

The water circulating through the rocks extracts from them by chemical dissolution of the minerals which in this case are chemical elements in the ionic form, such as sodium, potassium, calcium, magnesium, iron, silicon, aluminum, etc., and the foregoing properties may provide therapeutic benefits or simply effects favorable to human health. However, the chemical dissolution of certain minerals, usually sulfides, can lead to the concentration of toxic chemical elements, such as arsenic (As) and lead (Pb), in aquifers and their contamination, with serious consequences for human health.

An example of this is the arsenic contamination of water used for human consumption from shallow wells in Bangladesh and South India (Charlet and Polya 2006; Polya and Charlet 2009). In Bangladesh alone, arsenic-contaminated groundwater affects between 35 and 75 million people (Chen et al. 2009). More than 95% of the population now uses groundwater from about 10 (ten) million tube wells, and about 60% of these wells along the Ganges-Brahmaputra river system in Bangladesh are affected by As levels exceeding the WHO limit (Ahmed et al. 2004). Arsenic pollution is also of concern in other parts of the world.

About 6 (six) million people are at risk in West Bengal in India (Haque et al. 2003).

High concentrations of arsenic, adsorbed on iron oxides and hydroxides, occur naturally in the sediments of the Ganges Delta, and anthropogenic processes led to the mobilization of arsenic into almost superficial aquifers. About 20 (twenty) million people consume water contaminated with As, and their health is exposed to serious concerns. Chronic As poisoning leads to As accumulation in the skin, hair, and nails, an accumulation that results in symptoms such as strong pigmentation of hands and feet (keratosis), high blood pressure, and neurological dysfunctions (Chen et al. 2009).

The maximum levels of arsenic (the primary sources of which may be natural or anthropogenic, in this case from industrial pollution) and lead contamination (the primary sources of which are fuel, paint, and metal according to the WHO (World Health Organization), that could be present in water for human consumption are 0.01 mg/L and 0.01 mg/L, respectively.

In Portugal, for instance, relatively high concentrations of arsenic have been reported in some villages where the supply is made from groundwater abstractions that travel through fractures filled with arsenic-bearing sulfides, such as *arsenopyrite* (FeAsS) and *arsenic pyrite* (FeS_2). Anomalous levels of arsenic have been reported in waters consumed in certain places in the municipalities of Baião, Valbom, Vila Flor, and Ponte de Sor.

A note on the interaction of water/minerals to which there may be associated danger to ecosystems and to human health, for example the interaction of the waste or bargain of mining activity deposited and accumulated in so-called mine wastes located in the vicinity of the mines. Hazard can be particularly serious when mines are either deactivated or abandoned. Such wastes which are solid and liquid by-products from mining, mineral processing, and metallurgical extraction, as a rule, have no economic value. In many situations the residues of the mines being exposed to the atmosphere, hydrosphere, and microorganism conditions generate acidic effluents with high concentration of sulfate and metals (when the residues contain sulfides, the pH can show values of 3–5) or alternatively alkaline, metal, and metalloid solutions (Fe, Al, Cu, Zn, Cd, Pb, Ni, Co, Cr, As, Sb, Mo, U, and F) potentially toxic to humans and ecosystems when discharges rivers, lakes, and oceans (Hudson-Edwards et al. 2011; Nordstrom 2011).

Plumlee and Morman (2011) discuss the factors influencing the effects on human health of "mine wastes," in particular lead, mercury, and arsenic.

It should be noted that the extractive industry can have a strong impact on water quality and, consequently, on human health. Effectively, the process of remobilization of the mineralized geological materials and the concentration of the useful minerals is often by the action of the water that, of course, can by chemical leaching and dissolution start to include potentially toxic and polluting chemical elements for the ecosystems and indirectly for the man's health. Also, the use of fertilizers and pesticides in agriculture is a source of pollution of surface water and groundwater.

Nitrates, whose primary source is agricultural activity, are another possible contaminant of water for human consumption. The maximum levels of nitrate contamination allowed by both the EU (European Union) and the WHO (World Health Organization) are 50 mg/L. Also, phosphates, whose primary sources are the agrochemicals, are another possible contaminant.

About half of the world's population has water shortages and is confronted with water quality issues from vulnerable resources such as rivers, lakes, ponds, and shallow wells (WHO/UNICEF 2010).

A recognized international specialist in groundwater, the Spanish Ramon Llamas (2015), considers water scarcity today as a myth and criticizes the "hydrosquizophrenia" that prevails in many countries and for which there is still no known cure. According to Ramón Llamas, the problem lies in the mismanagement of aquifers and the inefficient use of water in unprofitable economic activities, such as irrigation of low-value agricultural products, warns the expert on the political use of water, and he states that the desalination of seawater has been a failure from the point of view of its agricultural use, when in many coastal regions the desalinated water could be used preferentially to groundwater. This is not only because the unit cost of desalinated water is significantly higher than the cost of groundwater, whose quality is degraded by the use of agrochemicals (fertilizers, insecticides, and fungicides), marine intrusion, etc. Ramón Llamas also states that the failure of construction in Spain of 20 (twenty) desalination plants whose water would be for agricultural use was due to the high cost of water for this purpose. However, the cost of desalinated water is already bearable when the goal is urban use.

The worldwide shortage of water for human consumption could be balanced by demineralization/desalinization of seawater and brackish water using the process called reverse osmosis that unlike natural osmosis requires the input of an external pressure to drive the water flow in the opposite direction (Crittenden et al. 2012).

In Portugal 594 million m^3 of drinking water is produced for consumption, and 13,782 km of pipelines are installed to transport this water. In 2016, ERSAR (the Portuguese Water and Waste Services Regulatory Body) estimated that 243,017 homes on the mainland are not connected to public water supply networks and use alternative sources of water supply, wells, and bottled water.

The coverage rate, i.e., the water from the public water supply arriving at homes, was estimated at 96%, and the coverage rate for wastewater treatment was estimated at 83%. Bringing piped water to small, widely dispersed settlements in the territory is difficult and very expensive. The water pipes for public supply then comprised 100,000 km.

Of course, these alternative sources may involve health risks due to possible microbiological contamination and chemical contamination; this is linked to the use of pesticides and fertilizers in agricultural practices, in the last case of nitrogenous and phosphate nature, and also to the presence of heavy metals. In these cases, the control of water quality is the responsibility of the consumer, whereby such control may not exist. Periodic analyses should be done to avoid exposure to contamination.

There are diseases that are associated with lack of drinking water quality, such as hepatitis A and B and typhoid fever.

Water disinfection is an issue of paramount importance in terms of public health, since most of outbreaks of disease come as a result of water- and food-borne enteric bacteria. Among them, typhoid and food poisoning (*Salmonella typhi*), dysentery and diarrhea (*Escherichia coli*), and cholera (*Vibrio cholera*) are enhanced. The virulence of these pathogens is so high that it is one of the main sources of death in the developing world. Thus, it has been reported that worldwide 1.3 million deaths of children are attributed to diarrheal illness each year.

According to the Portuguese DGS (General Directorate of Health) in 2012, only 10 cases of hepatitis A were registered, when in 1980 3000 cases were diagnosed. From a bacteriological point of view, the treated water should not contain coliform bacteria as is the case of enteric bacterium *E. coli* whose presence is indicative of fecal contamination, and the index NMP (most likely number of pathogenic microorganisms present in 100 ml water) should be less than 1.

Water must be made safe to drink, and an important step in ensuring water safety is disinfection. Disinfectants are added to water to kill disease-causing microorganisms. Groundwater sources can be disinfected by "The Water Treatment Rule," which requires public water systems for disinfection. Chlorination, ozone, ultraviolet light, and chloramines are primary methods for disinfection (Ishaq et al. 2018).

The EPA (Environmental Protection Agency) of the USA established in "The Water Treatment Rule" the minimum treatment requirements for public water systems using surface water as supply sources. Actually, chlorine is the most used chemical agent for water disinfection due to its low cost, effectiveness, and their extra protection against regrowth of pathogens and bacteria (Amin et al. 2014). Nevertheless, chlorine has received negative publicity, mainly due to the discovery that chlorination of water containing organic compounds could lead to the formation of trihalomethanes (THMs), which are suspected of having detrimental health effects (Nieuwenhuijsen et al. 2009; Villanueva et al. 2007).

On the other hand, some microorganisms have developed a special chlorine-induced antibiotic resistance in such a way that high dosage of the disinfectant in the water treatment is required (Yuan et al. 2015). Ozone and the use of membranes filters (Wang et al. 2015; Nassar et al. 2012) are alternative methods. The adsorption technique is the most sustainable alternative to the chemical agents to remove pathogens from potable water and wastewater due to its high simplicity, low-cost operation, high efficiency, as well as ease of regeneration. Among the adsorbents developed in recent years, *hydrotalcites* (Jin et al. 2007), metallic nanoparticles (Deng et al. 2014), have emerged as potential alternatives to chlorine for the removal of pathogenic organisms from water.

Pichel et al. (2019) present an interesting review on the conventional technologies being applied at medium to large scales to purify water and emerging technologies currently in development. The authors describe the merits, demerits, and limitations of the technologies, and they put a particular focus on solar disinfection, including a novel technology recently developed in this field.

In Europe water is considered "safe water" if it is monitored in line with European standards and whose analytical results meet the limits imposed. In the mainland of Portugal, ERSAR is responsible for regulating and supervising the quality of water for human consumption.

As in minerals *strictu sensu* or minerals *s.s*, in general, there are no two natural mineral waters alike with each water having a genetic signature or DNA, depending on its hydrobiochemochemical composition. Today, the chemical, physical, or physicochemical properties of natural mineral waters are relatively well known, as is not the case with a microbiological component also called *microbiota* or *microbiome*. In the microbiological component, only the pathogenic microorganisms (due to the negative impacts they have on human health) have been studied. The other microorganisms and their metabolites can be factors justifying the therapeutic properties of mineromedicinal mineral waters. The *microbio*ta of a natural mineral water is the bacterial, pathogenic, and nonpathogenic flora, which is very constant, which contains, at the outlet of the spring, flora whose qualitative and quantitative composition must be controlled through periodic analyzes (Directive 2009/54/EC).

The spring waters certified as *bacteriologically pure* are considered to be best termed as *pathogen germ-free* waters. Even so, several bacterial species can be identified by genomic sequential analysis. The overall nonpathogenic bacterial populations of one spring water, comprehensively termed microbiota, may be responsible for its regenerative properties. These properties may be related to the production of so far unknown substances that promote regeneration, probably in synergy with macro- and micromineral elements of the spring water (Pellegatta et al. 2016). The role of microbiota in controlling the balance between health and disease is a current topic of study due to its potential to be used for novel therapeutic approaches (Belizário and Napolitano 2015).

Nicolleti et al. (2017) have confirmed the ex vivo regenerative effects of a spring water, in a human ex vivo experimental model in the context of physiological wound healing using filtered Comano spring water in Italy. Previous experiments have indicated that the Italian calcium magnesium bicarbonate-based Comano spring water improves skin regeneration which was possibly associated with the native nonpathogenic bacterial flora (Faga et al. 2012).

The use of *natural mineral water*, *associated natural resources*, and *thermal tourism* are important contributions to the economy of the region where the *natural mineral water* occurs.

As has been aforesaid, *spring water* is a water of underground circulation and bacteriologically appropriate in its natural state for human consumption or health care. In Portugal, *spring water*s belong to the private domain, its use requiring an exploitation license issued by the local and regional administration.

With regard to *natural mineral waters* and *spring waters*, Portugal has a large diversity of waters, still (i.e., without natural gas), gasocarbon (i.e., bearing gas, CO_2, natural), and carbonated (i.e., bearing gas CO_2, artificial), which are marketed bottled.

Already in 1930, the eminent chemist Charles Lepierre in his book "Chimie et Physico-Chimie des Eaux (Le Portugal Hydrologique et Climatic)" said:

> Portugal, in proportion to its surface area and its population, is one of the richest countries in the world, in what concerns the variety and number of its mineral water springs.

In continental or mainland Portugal, 33 (thirty-three) brands of mineral water are known for bottling, marketing, and drinking, 18 (eighteen) classified as *natural mineral water*, and 15 (fifteen) classified as *spring water*. Among the bottled still *natural mineral waters*, the following stand out: Alardo, Fastio, São Cristovão, Vitalis, Luso, Penacova, and Monchique. Also, among the still flowing *spring waters*, the following stand out: Caramulo, Cruzeiro, Glaciar, Serra da Estrela, and Serrana. In addition, within the natural gas-rich mineral waters, the water of Pedras Salgadas stands out; the carbon dioxide it contains is 100% natural. Pedras Salgadas (Pedras Salgadas-Vila Pouca de Aguiar) is a singular natural mineral water classified as sodium bicarbonate water, HCO_3, Na, and DR (dry residue determined at 180 °C) contents being 1983 mg/L, 577 mg/L, and 2807 mg/L, respectively, and it is a current suitable drink to be taken after a substantial meal. The so-called carbonated waters are those to which carbon dioxide of origin other than the carbonic gas of the aquifer from which the water is supplied has been added.

The bottles of all bottled waters should show a label that allows the consumers to have enough information to know the physicochemical characteristics of the water they will ingest. The most relevant physical and chemical parameters (pH, total mineralization, and total dissolved salts) and the contents of the main anions and cations of the water should be indicated on the bottle label in addition to the commercial name, place of exploitation, and name of the source where it was extracted.

Bottled drinking water, both natural mineral water and spring water, has to be "clearness or limpidness, odorless, tasteless, colorless and harmless, that is devoid of pathogenic microorganisms and harmful chemicals to humans" and "safe" on the basis of established microbiological, physical, and chemical parameters (Quattrini et al. 2016).

The book *Geochemistry of Europa Bottled Water* published in 2010 by Borntrager Science, by Stuttgart, Reimann C, and Birke M (eds.), was the first state-of-the-art overview of the chemistry of groundwaters from 40 (forty) European countries from Portugal to Russia, measured on 1785 bottled water samples from 1247 wells representing 884 locations plus additional 500 tap water samples acquired in 2008 by the network of EuroGeoSurveys experts all across Europe. The book presents a comprehensive internally consistent overview of the natural distribution and variation of the determined chemical elements and additional state parameters of groundwater at the European scale. Most elements show a very wide range – usually 3–4 but up to 7 orders of magnitude – of natural variation of their concentration. Data are interpreted in terms of their origin, considering hydrochemical parameters, such as the influence of soil, vegetation cover, and mixing with deep waters, as well as other factors (bottling effects, leaching from bottles). The authors also provide an overview of the legal framework, that any bottled water sold in the European Union must comply with. It includes a comprehensive compilation of current drinking water action levels in European countries, limiting values of the European Drinking/Mineral/Natural Mineral Water directives (1998/83/EC, 2003/40/EC, 2009/54/EC), and legislation in effect in 26 individual European countries, and for comparison those of the FAO, and in effect in the USA (EPA, maximum contaminant levels [MCA]).

In recent times many studies have focused attention on the safety of bottled mineral water, in particular on the migration of chemicals from plastic containers to water. Plasticizers (additives used to impart flexibility and handling properties to several kinds of plastics) and *endocrine disruptors* (Eds – chemicals that interfere with function of the endocrine system) (Pinto and Reali 2009) are the main compounds involved in adverse effects on human health. Among these are the plasticizers like the Di(2-ethylhexyl)phthalate (DEHP) that is widely used as plasticizer and is also present in PET bottles (Bosnir et al. 2003). Polyethylene terephthalate (PET) is a material chemical inactive, but some in vitro studies proved that storage conditions (like exposure to sunlight and high temperature) may contribute to the release of chemicals from bottles to water (Biscardi et al. 2003).

The consumption of bottled mineral waters has greatly increased during the past few years, worldwide. The consumption of bottled water has been increasing all over the world. In Portugal, currently, the statistical data point to the consumption of 110 liters/inhabitant/year. And, about 57 (fifty-seven) million liters are exported, with Angola being the largest market. The bottled waters comprise natural mineral waters and spring waters, contributing the first with about 210 (two hundred ten) million euros for the national economy, with the second contributing with about 60 (sixty) million euros.

13.4 Water as an Essential Constituent of the Human Body and as a Health Conditioner

13.4.1 Basic Information

Water contributes significantly to health and good health, and is the essence of development. However, water's protective role is largely unseen and taken for granted in the wealthier countries. Its contribution to health is directly within households through food and nutrition and indirectly as a means of maintaining a healthy, diverse environment. These two precious resources – water and health – together could enhance prospects for development.

In humans, about 70% of body weight is represented by total body water (TBW), distributed into intracellular and extracellular fluid compartments, which contain about 65% and 35% of total body water, respectively.

Water is involved in many bodily functions, since it serves as a carrier of nutrients and substances in the circulatory system. Furthermore, water is the vehicle to excrete products and eliminate waste and toxins, and it also lubricates and provides structural supports to tissues and joints. However, there is no efficient mechanism for the body's water storage; therefore, a constant supply of fluids is needed to maintain water content. Water is present in all cells of the human body (in addition to water, cells also contain proteins, carbohydrates, lipids, and other compounds), in the intercellular fluid and also in the so-called organic fluids (blood plasma, urine, lymph, etc.). Water is the main vehicle for transporting nutrients and other substances into the circulatory system and is also the vehicle for the elimination of metabolites and toxins through the vascular, renal, and hepatic systems.

Table 13.8 Concentrations of minerals in the blood serum and in the human body (Peacock (2010); Bloodbook (2013); FNB (2005); Abramowitz et al. (2012); Bowman and Russell (2006); NSFA (2013); Deng et al. (2008); Wallach (2007), (*In*: Ferrante et al. 2015))

Minerals	Normal range of concentrations in serum	Total content in human body	RDD
Calcium (Ca)	8.8–10.4 mg/dL	1000–1200 g	1000 mg
Magnesium (Mg)	3.7–4.9 mg/dL	25–30 g	300
Bicarbonate (HCO_3)	110–140 mg/dL		
Sulfate (SO_4)	27–30 mg/dL		
Sodium (Na)	331–335 mg/dL	90–100 g	<2 g (0.18 g minimum required)
Potassium (K)	13.7–19.6 mg/dL	140–225 g	3 g
Phosphorous (P)	3.0–4.5 mg/dL	750–850 g	700 mg
Chloride (Cl)	350–376 mg/dL	82 g	<3 g
Iron (Fe)		2.1–2.8 g	12 mg
Copper (Cu)	70–150μg/dL	70–80 mg	0.8 mg
Molybdenum (Mo)			45μg
Zinc (Zn)	0.06–0.12 mg/dL	1.5–2.5 g	8 mg
Chromium (Cr)	5–55μg/dL	6 mg	100μg
pH	7.34–7.45		
Ca/Mg	2.1–3.1:1		3:1
Na/Ca	32–35:1		2:1
Na/K	20–40:1		0.67:1
Ca/P	2.3–8.5:1		1.4:1
Na/Mg	68–84:1		0.6 (min.)–7:1
(Na + K)/(Cl + HCO_3)	3.0–11:1		

Table 13.9 Percentage by weight and volume of water in the major body tissues of an adult weighing 70 kg (*In*: Failde 2008a, b)

Tissue	Water (%)	Water (L)
Kidney	83	0.25
Lung	80	0.40
Blood	76	4.65
Cerebrum	75	1
Muscle	76	22.10
Skin	72	10
Bone	22	2.45

Table 13.10 Chemical composition of intracellular and extracellular liquids

Elements/compounds	Intracellular liquid	Extracellular liquid
Sodium	10 mmol/L	142 mmol/L
Potassium	156	4
Calcium	3	5
Magnesium	26	2
Total	**195** mmol/L	**153** mmol/L
Chlorine	2 mmol/L	103 mmol/L
Bicarbonate	8	26
Phosphate	95	2
Organic acids	>20	6
Proteins	55	16
Total	**>180** mmol/L	**153** mmol/L

About 70% by weight of the human body consists of water, and there are organs that contain more water than others. In a man weighing 65–70 kg, there are 40 to 42 (forty to forty-two) liters of water, about 25 (twenty-five) liters inside the cells, called intracellular water, and about 17 (seventeen) liters on the outside of the cells, called extracellular water, which comprises about 13 (thirteen) liters of the so-called interstitial water and about 4 liters of the so-called intravascular water.

In intravascular water, in the case of blood, it contains about 90% of water, mainly in blood plasma, which in addition to water contains red blood cells and white blood cells, platelets, minerals (Na, K, Ca, Mg, Zn, Cr, P, etc.), proteins, and glucose.

Minerals are important constituents of both water and the human body. In this, in quantitative terms, the total of minerals corresponds to about 5% of the mass of the human body. Table 13.8 shows the ranges of total concentrations of the major minerals in the human body, the range of concentrations of the major minerals in the blood serum, and the recommended daily dose (RDD) or recommended daily intake (RDI) values for an adult with the weight of 70 kg.

Table 13.9 shows the percentage by weight and volume of water contained in the main tissues of an adult body weighing 70 kg.

Men's body has about 15% more water than women's body. And, from the relative point of view, it is in the body of the newly born baby that the water content is higher (estimated at about 90%). Intracellular and extracellular water or body fluids have distinct compositions and concentrations in terms of cations, anions, and other dissolved compounds. According to Teixeira (2009), cell membranes are fundamentally responsible for regulating and controlling ion exchange between *extracellular* and *intracellular* fluids.

Table 13.10 shows the concentrations in millimoles per liter (mmol/L) of the major cations and anions of body waters.

A state of good health requires intracellular water and extracellular water to be more or less in dynamic equilibrium; the same must occur with chemical elements and compounds, that is, the search for electrolyte equilibrium.

An active adult requires about 30–35 ml/kg/day (milliliters per kilo per day) of water, meaning that an adult weighing 70 kg should drink a little more than 2 L/day. In a normal diet, of the total water intake, 20–25% comes from solid foods and 75–80% comes from liquid foods.

The lack of water in the human body can lead to dehydration. Signs of dehydration can be classified into two types: mild or moderate (drowsiness and tiredness, headache, dizziness, dry mouth, thirst, muscle weakness, and decreased urine production) and severe (severe drowsiness, irritability, fever, dry mouth, dry skin, very dry mucous membranes, extreme thirst, tachycardia, lack of sweating, i.e., sweat production, and little or none in urine). Even if you are not thirsty, it is essential to drink water to meet the hydration needs that increase with the heat because the body loses more water in the mechanisms of counter-regulation of body temperature.

Under normal conditions, body water volume may fluctuate less than 1% per day. A state of dehydration due to losses equal to or greater than 2% of body water volume may result in impairment of cognitive function, physical performance, and fatigue symptoms.

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