THE SCIENCE OF BEVERAGES
VOLUME 4

BOTTLED AND PACKAGED WATER

Edited by
Alexandru Mihai Grumezescu
Alina Maria Holban

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SERIES PREFACE

Food and beverage industry accounts among the most developed sectors, being constantly changing. Even though a basic beverage industry could be found in every area of the globe, particular aspects in beverage production, processing, and consumption are identified in some geographic zones. An impressive progress has recently been observed in both traditional and modern beverage industries and these advances are leading beverages to a new era. Along with the cutting-edge technologies, developed to bring innovation and improve beverage industry, some other human-related changes also have a great impact on the development of such products. Emerging diseases with a high prevalence in the present, as well as a completely different lifestyle of the population in recent years have led to particular needs and preferences in terms of food and beverages. Advances in the production and processing of beverages have allowed for the development of personalized products to serve for a better health of overall population or for a particular class of individuals. Also, recent advances in the management of beverages offer the possibility to decrease any side effects associated with such an important industry, such as decreased pollution rates and improved recycling of all materials involved in beverage design and processing, while providing better quality products.

Beverages engineering has emerged in such way that we are now able to obtain specifically designed content beverages, such as nutritive products for children, decreased sugar content juices, energy drinks, and beverages with additionally added health-promoting factors. However, with the immense development of beverage processing technologies and because of their wide versatility, numerous products with questionable quality and unknown health impact have been also produced. Such products, despite their damaging health effect, gained a great success in particular population groups (i.e., children) because of some attractive properties, such as taste, smell, and color.

Nonetheless, engineering offered the possibility to obtain not only the innovative beverages but also packaging materials and contamination sensors useful in food and beverages quality and security sectors. Smart materials able to detect contamination or temperature differences which could impact food quality and even pose a hazardous situation for the consumer were recently developed and some are already utilized in packaging and food preservation.

This 20-volume series has emerged from the need to reveal the current situation in beverage industry and to highlight the progress of the last years, bringing together most recent technological innovations while discussing present and future trends. The series aims to increase awareness of the great variety of new tools developed for traditional and modern beverage products and also to discuss their potential health effects.

All volumes are clearly illustrated and contain chapters contributed by highly reputed authors, working in the field of beverage science, engineering, or biotechnology. Manuscripts are designed to provide necessary basic information in order to understand specific processes and novel technologies presented within the thematic volumes.

Volume 1, entitled *Production and management of beverages*, offers a recent perspective regarding the production of main types of alcoholic and nonalcoholic beverages. Current management approaches in traditional and industrial beverages are also dissected within this volume.

In Volume 2, *Processing and sustainability of beverages*, novel information regarding the processing technologies and perspectives for a sustainable beverage industry are given.

Third volume, entitled *Engineering tools in beverage industry* dissects the newest advances made in beverage engineering, highlighting cutting-edge tools and recently developed processes to obtain modern and improved beverages.

Volume 4 presents updated information regarding *Bottled and packaged waters*. In this volume are discussed some wide interest problems, such as drinking water processing and security, contaminants, pollution and quality control of bottled waters, and advances made to obtain innovative water packaging.

Volume 5, *Fermented beverages*, deals with the description of traditional and recent technologies utilized in the industry of fermented beverages, highlighting the high impact of such products on consumer health. Because of their great beneficial effects, fermented products still represent an important industrial and research domain.

Volume 6 discusses recent progress in the industry of *Nonalcoholic beverages*. Teas and functional nonalcoholic beverages, as well as their impact on current beverage industry and traditional medicine are discussed.

In Volume 7, entitled *Alcoholic beverages*, recent tools and technologies in the manufacturing of alcoholic drinks are presented. Updated information is given about traditional and industrial spirits production and examples of current technologies in wine and beer industry are dissected.

Volume 8 deals with recent progress made in the field of *Caffeinated and cocoa-based beverages*. This volume presents the great variety of such popular products and offers new information regarding recent technologies, safety, and quality aspects as well as their impact on health. Also, recent data regarding the molecular technologies and genetic aspects in coffee useful for the development of high-quality raw materials could be found here.

In Volume 9, entitled *Milk-based beverages*, current status, developments, and consumers trends in milk-related products are discussed. Milk-based products represent an important industry and tools are constantly been developed to fit the versatile preferences of consumers and also nutritional and medical needs.

Volume 10, *Sports and energy drinks*, deals with the recent advances and health impact of sports and energy beverages, which became a flourishing industry in the recent years.

In Volume 11, main novelties in the field of *Functional and medicinal beverages*, as well as perspective of their use for future personalized medicine are given.

Volume 12 gives an updated overview regarding *Nutrients in beverages*. Types, production, intake, and health impact of nutrients in various beverage formulations are dissected through this volume.

In Volume 13, advances in the field of *Natural beverages* are provided, along with their great variety, impact on consumer health, and current and future beverage industry developments.

Volume 14, *Value-added Ingredients and enrichments of beverages*, talks about a relatively recently developed field which is currently widely investigated, namely the food and beverage enrichments. Novel technologies of extraction and production of enrichments, their variety, as well as their impact on product quality and consumers effects are dissected here.

Volume 15, *Preservatives and preservation approaches in beverages,* offers a wide perspective regarding conventional and innovative preservation methods in beverages, as well as main preservatives developed in recent years.

In Volume 16, *Trends in beverage packaging*, the most recent advances in the design of beverage packaging and novel materials designed to promote the content quality and freshness are presented.

Volume 17 is entitled *Quality control in beverage industry*. In this volume are discussed the newest tools and approaches in quality monitoring and product development in order to obtain advanced beverages.

Volume 18, *Safety issues in beverage production*, presents general aspects in safety control of beverages. Here, the readers can find not only the updated information regarding contaminants and risk factors in beverage production, but also novel tools for accurate detection and control.

Volume 19, *Biotechnological progress and beverage consumption*, reveals novel tools used for advanced biotechnology in beverage industry production.

Finally, Volume 20 entitled *Nanoengineering in beverage industry* take the readers into the nanotechnology world, while highlighting important progress made in the field of nanosized materials science aiming to obtain tools for a future beverage industry.

This 20-volume series is intended especially for researchers in the field of food and beverages, and also biotechnologists, industrial representatives interested in innovation, academic staff and students in food science, engineering, biology, and chemistry-related fields, pharmacology and medicine, and is a useful and updated resource for any reader interested to find the basics and recent innovations in the most investigated fields in beverage engineering.

Alexandru Mihai Grumezescu
Alina Maria Holban

PREFACE

Drinking water is the most valuable resource on the planet. In numerous areas, this natural resource is a rare occurrence or its available quality is poor. For this reason, strategies for water purification and for checking and increasing its availability and quality are intensively investigated. Currently, bottled and packaged water represents a huge industry, with a great economical, ecological, and social impact. The purpose of this book is to bring together recent findings on the bottled and packaged water research, exposing the current situation worldwide, while emphasizing the novel technologies employed to obtain improved quality waters to fulfill the requirements of a wide variety of consumers.

This volume contains 15 chapters prepared by outstanding authors from Poland, India, Romania, Pakistan, Italy, Germany, Portugal, Malaysia, and Nigeria.

The selected manuscripts are clearly illustrated and contain accessible information for a wide audience, especially food and beverage scientists, engineers, biotechnologists, biochemists, industrial companies, students and also any reader interested in learning about the most interesting and recent advances in the field of beverage science.

Chapter 1, *Mineral and bottled water as natural beverages*, by Nguyen Dinh Chau et al., describes the major bottled, natural mineral, and therapeutic water occurring worldwide. The interdependences between the concentrations of the chemical components in the water and some heavy and radioactive elements are also described. In this chapter the hazard and problems connected with the presence of the heavy and radioactive elements are considered.

Chapter 2, *The world around bottled water*, by Bhawana Jain et al., addresses every aspect of bottled water in the current global context, from sales, consumption, cons-pros, etc. to environmental concerns.

In Chapter 3, *Study of water quality of packaged and municipal supply drinking water with performance evaluation of stand-alone filters*, Pankaj Kumar Roy et al. assess the bacteriological and physiochemical quality of bottled and bubble-top-can packaged drinking water (PDW) sold in Kolkata and surrounding areas and compared with that of Kolkata Municipal Corporation (KMC) supply water. The conclusion of their study is that KMC supply water can be a good alternative for drinking purpose other than the PDW available in the local market.

Chapter 4, W*ater purification technologies*, by Asif Ahmad et al., illustrates the principles, functioning, and the selection suitability for water purification technologies and presents recent research carried out in this field.

Chapter 5, Multielement and isotopic characterization of bottled mineral waters on the Romanian market, by Cezara Voica, analyzes the major elements and stable isotopes of oxygen and hydrogen in various types of bottled water (domestic and foreign) commercially available in Romania in order to classify the water types and identify their origins. Major mineral contents of waters established were Ca (5.41–293.7 $\mathrm{mg\,L^{-1}}$), Mg (0.89–189.4 $\mathrm{mg\,L^{-1}}$), and K (0.032–42.17 $\mathrm{mg\,L^{-1}}$). For some trace elements, the ranges of concentration were (in $\mu\mathrm{g\,L^{-1}}$): <0.001–0.077 for Cd; < 0.001–0.067 for Pb; < 0.001–305.608 for Mn; 0.222–10.520 for Ni; < 0.001–13.908 for Zn; <0.001–58.778 for Al. The hydrogen and oxygen isotope ratios of Romanian bottled water range from −87.7‰ to −65.0‰, and between −12.9‰ and −9.2‰, respectively. The obtained isotopic values fall in the normal range for meteoric waters, clustering along the meteoric water line.

Chapter 6, Evaluation of water quality available for direct use and in beverages in Agra (India), by Ashish Kumar et al., presents a comprehensive evaluation and comparison of the fluoride content along with some other parameters of a range of bottled water and ground and tap water considering risks of systemic fluoride exposure. In all, 15 brands of bottled water (10 bottled + 5 pouched) commercially available in Agra city, two samples of tap water from different locations, and four ground water samples were examined for fluoride content along with some other parameters such as hardness, pH, conductivity, turbidity, TDS and DO for detailed evaluation of water quality available for direct use and in other beverages.

Chapter 7, *Chemical sensors for water potability assessment*, by Larisa Lvova et al., reviews the recent advances in chemical sensors for potable water analysis. The working principles of the most diffused sensors are illustrated and discussed. The attention is focused on optical and electrochemical sensors, either operated alone or as element of multisensor and multitransduction systems. The performance of these sensors and sensor systems have been demonstrated for the detection of several pollutants in water, such as transition and heavy metals, algal toxins, herbicides, and pesticides among others. A critical outlook about the use of multisensor system compared to selective sensors in natural samples is also presented.

Chapter 8, *Microbiological and chemical characterization of bottled waters*, by Mihaela Magdalena Mitache et al., presents the most applied and investigated physical, chemical, and microbiological parameters and methods used for the assessment of bottled water quality.

Chapter 9, *Advanced biodegradable materials for water and beverages packaging*, by Irina Gheorghe et al., aims to reveal the beverage packaging advances, focusing on the chemical modification of packaging materials and the development of new advanced polymers, which cannot influence the product qualities or negatively impact the environment.

Chapter 10, *Contribution of mineral and tap water to the dietary intake of As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn by humans*, by Ewald Schnug et al., summarizes the contribution of water and solid food in relation to the nutritional style on the intake of As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn. It seems that consumers ingest significant amounts of U with mineral and potable water while the intake by solid food is distinctly lower and shows a much smaller bandwidth. Agricultural practices contribute worldwide to an enrichment of U in water bodies which poses a serious threat to the water quality of mineral water.

Chapter 11, *Significance of geographical, hydrogeological, and hydrogeochemical origin for the elemental composition of bottled German mineral waters*, by Ewald Schnug et al., aims to allocate water provenances on the basis of their elemental composition in relation to stratigraphic, hydrogeological and hydrogeochemical classifications thus providing additional value to the existing classification schemes. Analysis of geographical classes reveals that high concentrations of Be, Cs, Er, F, Ge, Lu, Mo, Sb, Si, Tm, U, Yb, and HCO_3 can be expected in geologically older rocks, specifically from the Proterozoic. Hydrogeological classes reveal that high concentrations of La and Nb can be expected in waters from sources in the lowlands or in regions with unconsolidated rocks. Rare earth elements were ranked first for discriminating between classes of all three classification systems investigated in this study. In total 16 elements proved to be suitable for discrimination, with Dy, Er, Gd, Lu, Sm, and Tm being identified most frequently.

Chapter 12, *Characterization of bioactive compounds in flavored waters and fruit juices*, by M. Fátima Barroso et al., reviews the characterization of bioactive compounds in flavored waters and fruit juices. Furthermore, it is also intended to describe selective assays for bioactive compound assessment, such as spectrophotometric, DNA-based sensors, and chromatographic methods.

Chapter 13, entitled *Plants infused water as preferred healthy drinks*, prepared by Kokila Thiagarajah et al., deals with phytochemicals that can be extracted from fruits, vegetables, and herbs as well as emphasizing the health benefits derived from consumption of this plant-infused water as potential preferred healthy drinks. Infused water is considered an alternative natural way of treating or preventing illness without any side effect unlike other commercialized medications.

Chapter 14, *Main microbiological pollutants of bottled waters and beverages*, by Carmen Curutiu et al., presents the main microbial contaminants of bottled water and the associated risk for waterborne/foodborne diseases. Although consumption of quality drinking water should be available to anyone, without any risk, in reality, for the people living in poor countries, safe water sources are often not an option. In order to eliminate the risk of disease, people prefer to use bottled water, or even bottle beverages, considering them uncontaminated, sterile products. However, evidences show that some microbial species belonging to autochthonous water microbiota or even pathogenic species may contaminate and could, in certain conditions, multiply beyond measure in the bottled products.

Chapter 15, *Industrial energy use and energy-saving potentials in Nigeria: case study of food manufacturing industries*, by Oyedepo Sunday Olayinka et al., reviews various patterns of energy consumption, highlights the sources of energy wastage, and suggested possible energy-saving techniques that could be employed to reduce energy waste in the food and beverage industries, including water processing. Results of this study revealed that the source of electrical energy in the food industries is mainly from generating set; this is due to the poor state of infrastructures in the power sector. The major factors that lead to energy waste in the industries are waste energy in boiler plant, use of second hand and ageing equipment, and lack of maintenance culture among others. This study concluded that adopting efficient energy-saving technologies can result in savings of about 10%–30% of the current average costs in the industries. The possible and effective energy-saving technologies are also discussed in this paper.

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MINERAL AND BOTTLED WATER AS NATURAL BEVERAGES

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1.1 Introduction

The concept of mineral water was first defined in 1911 at the International Balneological Congress in Bad Nauheim in Germany, and it was agreed that waters that have at least 1000 mg of minerals per liter will be considered to be mineral water. Based on the directive of the European Parliament and of the Council no. 2009/54/EC of 18 June 2009 on the exploitation and marketing of natural mineral water "Natural mineral water can be clearly distinguished from ordinary drinking water: (a) by its nature, which is characterized by its mineral content, trace elements or other constituents and, where appropriate, by certain effects; and (b) by its original purity, both characteristics having been preserved intact because of the underground origin of such water, which has been protected from all risk of pollution" (Directive, 2009).

A new phenomenon has recently been noticed worldwide, which involves an increase in applications for the production of bottled mineral water to be consumed in place of tap water. Steady year on year growth in its consumption has been observed. Such waters are recommended not only because of their specific taste characteristics and the content of various mineral compounds, but also because of the common conviction, which is prevailing among supporters of bottled waters, that their quality and wholesomeness are very good and generally do not raise as many concerns as tap water (Bodzek et al., 2017).

Nowadays, most consumers get their drinking water from three main sources: bottled water, tap water, and filtered water. As the trend toward a healthy lifestyle becomes increasingly popular, many mineral water brands are marketed in developed countries. The first functional water brands that are fortified with selected trace elements, vitamins, herbal extracts, or probiotics have also begun to emerge. A significant development of this industry in world markets was observed between 2002 and 2008, mainly as a result of the scale

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of production and sales of such products in the United States and in Asia (Tomaszewska et al., 2016).

Many countries have their own regulations and classifications of natural water and some of them have analyzed the legitimacy of consuming bottled water instead of tap water (Dinelli et al., 2012; Zamberlan da Silva et al., 2008; Platikanov et al., 2017). In the United States, bottled water is strictly regulated as a packaged food product by the US Food and Drug Administration (FDA) and bottled water is a safe, refreshing, convenient, and consistently reliable beverage choice. Under federal law, FDA regulations governing the safety and quality of bottled water are as stringent as the Environmental Protection Agency (EPA) regulations that govern tap water (BW, 2017).

The perception of why one should drink bottled water rather than tap water is based on the expectation that it will be of superior quality, more palatable, and free from health hazards (Rahman et al., 2017). However, bottled mineral water should be representative of the hydrogeochemical composition of groundwater, whereas tap water could derive from multiple sources such as groundwater or surface water including rivers and reservoirs (Dinelli et al., 2012). In fact, in every case it is natural water that is being analyzed.

The production of bottled water is monitored by the International Bottled Water Association (BW, 2017) and analyzed as:

- Drinking water—water placed in sterile containers used for human consumption. The additives in this water should be about 1% weight of the water.
- Mineral water—water that is made up of no <250-part-per-million of dissolved solids (minerals).
- Artesian well water—water from "a well that taps a confined aquifer in which the water level stands at some height above the top of the aquifer."
- Purified water—water that consists of distilled water or deionized water.
- Sparkling water—water that is carbonated.

The past 5 years have seen an increase in the per capita consumption of bottled water worldwide. Roughly 354 million liters of bottled water were sold in Mexico in 2016 and sales are expected to reach 356 million liters by 2018. Thailand's per capita consumption of bottled water has boosted from 26.3 gal in 2009 to 64.5 gal in 2015. In 2012, the global consumption of bottled water amounted to 288 billion liters and by 2017 people all over the world are expected to consume about 391 billion liters. In 2015, Mexico had the highest per capita consumption of bottled water in the world amounting to about 64.5 gal (Stat, 2017a). However, in 2016, the per capita consumption of the United States was 39.3 gal.

The bottled water industry is a strong supporter of our environment and our natural resources. Bottled water companies manage resources responsibly by investing in technology and in practices that improve water quality and conservation.

1.2 Physicochemical Properties of Mineral and Therapeutic Water and Its Roles in Daily Life

In many countries, there are specific regulations and rules of law used to classify groundwater. Water can be used for medicinal purposes if it naturally contains a minimum amount of at least one of the components (Gutenbrunner and Hildebrandt, 1998) cited in the regulations. In Japan (Altman, 2000), Poland (Kiełczawa, 2018), Germany, Iceland (Kristmannsdóttir and Björnsson, 2003), Italy (Andreassi and Flori, 1996), and Spain (Ledo, 1996), waters are classified by chemical character, temperature, and balneological properties. In the Polish regulations (RMH, 2011), natural waters are classified into water, mineral water, spring water, and table water. However, if groundwater is not contaminated and has natural variations in physical and chemical parameters and contains at least one specific component (pharmacodynamic factors) and/or has a temperature above 20°C, it is then considered to be therapeutic water (PGG, 2015). Moreover, whole mineral water (mineralization $>1\,\mathrm{g\,L^{-1}}$) can be medicinal water, regardless of whether it contains specific components (Table 1.1).

Table 1.1 Example of the Balneological Classification of Water in Poland

Total Dissolved Solids (TDS)	Temperature (°C)	Pharmacodynamic Factors—Specific Components	Chemical Type of Water
$\geq 1\,\mathrm{g\,L^{-1}}$—mineral	> 20—thermal water	$2\,\mathrm{mg\,F^{-}\,L^{-1}}$	Fluoride
$<1\,\mathrm{g\,L^{-1}}$—slightly mineralized	<20—cold water	$1\,\mathrm{mg\,I^{-}\,L^{-1}}$	Iodated
		$1\,\mathrm{mg\,S(II)\,L^{-1}}$	Sulfuric
		$70\,\mathrm{mg\,H_2SiO_3\,L^{-1}}$	Silica
		$10\,\mathrm{mg\,Fe(II)\,L^{-1}}$	Ironic
		$74\,\mathrm{Bq\,L^{-1}}$	Radon or radioactive
		$250\,\mathrm{mg\,L^{-1}}$ free CO_2	Carbonate
		$1000\,\mathrm{mg\,L^{-1}}$ free CO_2	CO_2-rich, carbonized

Based on PGG, 2015. Ustawa z dnia 9 czerwca 2011: Prawo geologiczne i górnicze (Act of June 9, 2011: Geological and Mining Law.

Many natural mineral waters are not characterized by strong concentrations of ionic components. For this reason, they are classified as lightly mineralized or oligo-mineral water. In many cases, they are called spring water and table water. These waters are valuable for their sedative (helping to reduce stress) properties (Altman, 2000).

Mineral water contains a combination of the main cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), anions (HCO_3^{-}, Cl^{-}, SO_4^{2-}) and specific compounds (which can determine the medicinal value of water) in varying amounts. These dissolved components bring various health benefits. Table 1.2 presents the recommendations for the treatment of different diseases depending on the type of mineral water (bicarbonate, chloride-sulfate).

Mineral water is generally an insignificant source of dietary iron, iodine, or fluoride. However, in some circumstances it can be a very major source. Iodine-rich groundwater has been found in several provinces of China (Wen et al., 2013), with iodine contents ranging up to 2800 $\mu g\,L^{-1}$ in Jiangsu Province (Zhao et al., 2000) and up to 4100 $\mu g\,L^{-1}$ in Shanxi Province (Tang et al., 2013). The human health risks from supplementing drinking water with iodine are negligible (Lewandowski et al., 2015); therefore, this approach is worthy of regulatory consideration. Thus, it appears reasonable to consider the use of mineral water fortified with iodine as a source of easily assimilated iodine.

Table 1.2 Therapeutic Effects and Recommendations for Thermal Treatment Depending on Type of Water

Main type of Mineral Water	Recommendations and Therapeutic Benefits
Bicarbonate water	– Especially in cardiovascular diseases, nervous exhaustion, autonomic nervous system imbalance, severe heart and circulatory illnesses, gout, and hepatic insufficiency – Opens the peripheral blood vessels, improving circulation
Sulfate and sulfur water	Chronic skin diseases, metabolic poisoning, gynecological disorders, rheumatism, liver and gastrointestinal complaints, osteoporosis, and nervous system disorders
Chloride water (brine)	Arthritis, rheumatism, nervous system diseases (central and peripheral), orthopedic, postoperative dysfunctions, gynecological and skin diseases, joint disorders, asthma, and respiratory problems

Based on Altman, N., 2000. Healing Springs. Healing Arts Press, Rochester, VT.

Mineral springs used for health range from primitive natural springs to developed facilities to commercialized centers. In many countries, this depends on the tradition of mineral spring use, culture, religion, economic conditions, and the political situation. The presence of specific components in mineral water determines its benefits when used for balneological and therapeutic purposes. Polish regulations specify the maximum admissible concentrations of ingredients that are undesirable in excessive amounts and of toxic ingredients in therapeutic water (Table 1.3).

In practice, the following types of water are recommended for inhalation purposes (Tomaszewska, 2018):

- chloride-sodium, iodide
- chloride-sodium bicarbonate-calcium at concentrations of up to 1.5%

The following types of water are used most frequently for bathing purposes:

- brines (chloride-sodium waters), iodide, and/or sulfide-hydrogen sulfide waters
- specific thermal waters: radon and sulfide-hydrogen sulfide waters.

Table 1.3 The Maximum Admissible Concentrations of Ingredients That Are Undesirable in Excessive Amounts and of Toxic Ingredients in Therapeutic Waters

	The Highest Admissible Concentrations		
Parameter	**Drinking Cure**	**Inhalation**	**Bathing**
B (mg L^{-1})	5.0	30.0	–
Cr (mg L^{-1})	0.01	0.01	–
Cd (mg L^{-1})	0.003	0.003	–
Ni (mg L^{-1})	0.03	0.03	–
Pb (mg L^{-1})	0.01	0.01	–
Hg (mg L^{-1})	0.001	0.001	–
Al (mg L^{-1})	0.1	0.1	–
Ba (mg L^{-1})	1.0	10.0	–

Based on RMH, 2006. Regulation of the Ministry of Health of 13 April 2006 concerning research necessary to determine the healing properties of natural medicinal raw materials and the healing properties of the climate, the criteria for their evaluation and the template of the certificate confirming these (Dz. U 2006 No 80 poz. 565).

Some mineral waters may be considered "dietary foods for special medical purposes" in their natural state. This includes natural waters or their concentrates containing ingredients such as iodides, fluorides, calcium, magnesium, and sodium in significant concentrations from the point of view of the physiological functions of the human body (Tomaszewska, 2018). At the same time, these waters or concentrates must not contain potentially toxic ingredients in concentrations considered harmful to health.

Alkaline mineral waters with low calcium content (so-called soft waters) and also with significant levels ($>100\,\mathrm{mg\,L^{-1}}$) of silicon compounds may be used in cosmetics, including in combination with plant extracts.

Currently, the market has stabilized and consumers are looking for healthy new natural products. Their expectations could in the future be met by beverages—natural functional water based on mineral waters. In 2016, private labels were the leading bottled still water brands in the United States with around 2.31 billion US dollars in sales, followed by Dasani, Aquafina, and Nestlé Pure Life. Moreover, the Coca-Cola-owned brand Dasani held a 9.9% share of the US bottled still water market. At the same time, Sparkling Ice was the second leading bottled sparkling water brand in the country, after private label brands. Around the same time, Danone, the Coca-Cola Company, and Nestlé SA were the best-selling bottled water companies worldwide (Stat, 2017b). In France, there are >200 brands of French bottled water (FW, 2017). The most popular brand in the world is "Perrier," which originates in Southern France (Nestle, 2017). The brand is widely known for its characteristic green, club-shaped bottle with white lettering. In the Polish market, most popular brands are natural mineral waters, for example, Muszynianka and Piwniczanka, but on the beverages water market, the following products are also offered:

- Zbyszko brand waters: Veroni Mineral Fit in six flavors: (1) lemon + vitamin C; (2) strawberry + calcium; (3) apple + zinc; (4) peach + fiber; (5) grapefruit + magnesium; and (6) coconut + L-carnitine (ABC Consulting, 2013).
- Ustronianka Sp. z o.o. brand waters: (1) with iodine; (2) with magnesium; (3) with calcium; and (4) with potassium (Ustronianka, 2017) www.ustronianka.com.pl/4-ustronianka_funkcjonalna.html).
- Jupik Aqua Sport water fortified with vitamins B12, B9, and B3 by Hoop Polska Sp. z o.o. (Hoop, 2017).
- Voda Naturalna Sp. z o.o.: water with collagen (Voda, 2017).

The first water fortified with iodine on the Polish market was launched in 2009 by Ustronianka Sp. z o.o. (Tomaszewska et al., 2016). The product was based on natural mineral water. It was water with a mineral content of approx. $507\,\mathrm{mg\,L^{-1}}$ and with low sodium content (6.4–7.1 mg Na/L), containing calcium ($90–117\,\mathrm{mg\,L^{-1}}$), magnesium ($16.5–21.3\,\mathrm{mg\,L^{-1}}$), potassium ($\sim 1\,\mathrm{mg\,L^{-1}}$), carbohydrates

(295–299 mg L^{-1}), sulfates (41.8–48.8 mg L^{-1}), and chlorides (21.1–26.7 mg L^{-1}) (MSW, 2011). It has been registered as a foodstuff intended for a particular nutritional use, recommended for pregnant women and lactating mothers, and also for those who require a low-sodium or sodium-free diet.

1.2.1 Selected Methods Used in the Measurement of the Chemical Composition of Mineral and Therapeutic Waters and the Radioactive Elements Occurring in Them

The quality of mineral water should be assessed through online measurements of the unstable physical parameters of water, that is, temperature and electrolytic conductivity, pH of water, and Eh. All of these parameters should be measured using the electrometric method immediately after sampling water from a well or spring. Inorganic components can be determined using the inductively coupled plasma mass spectrometry (ICP-MS) method. The scope of analysis included the determination of sodium, potassium, lithium, beryllium, calcium, magnesium, barium, strontium, iron, manganese, silver, zinc, copper, nickel, cobalt, lead, mercury, cadmium, selenium, antimony, aluminum, chromium, molybdenum, vanadium, zirconium, titanium, arsenic, thallium, tungsten, bromides, iodides, sulfates, phosphates, silica, and boron content. Chloride ion content and water alkalinity were determined by titration in accordance with accredited testing procedures (Witczak et al., 2013).

Measurements of total activity of radioactive α and β nuclides and the concentration of radon (^{222}Rn), uranium (^{238}U, ^{234}U), and radium (^{226}Ra, ^{228}Ra) isotopes were performed using an Alpha Spectrometer Model 7401 with a semiconductor detector as well as an alpha/beta detector with a Wallac Guardian 1414 liquid scintillation counter. Tritium concentration was estimated on an electrolyte-enriched sample using the liquid scintillation counting method and a Packard Model 2500 P TR/AB device. The following equation was used to calculate the doses (Chau and Michalec, 2009; IAEA, 1996; Tomaszewska and Bodzek, 2013):

$$D(g) = N \cdot \sum \eta_i \cdot W_i$$

where

D(g): annual effective dose equivalent (*g-person in the age group*) (mSv year^{-1}).

N: intake of water per person per year.

η_i: the age-dependent dose conversion factor (mSv Bq^{-1}) for the *i*th isotope, respectively.

W_i: the concentration of the given radioisotope ($\mathrm{Bq\,L^{-1}}$).

The values of η_i for different elements are found in the publications of the IAEA (1996). Table 1.4 shows the committed unit doses of four key isotopes of uranium and radium.

1.2.2 Occurrence of Heavy and Radioactive Elements in Mineral and Therapeutic Waters

1.2.2.1 Heavy Elements

Heavy elements are usually defined as elements with an atomic mass >40. The occurrence of heavy elements in water is often generated from leaching of the soil and rock minerals. In some regions, the content of heavy metals in water is significantly high; such anomalies are often probably connected with human activities. The conception model of the processes controlling the occurrence of heavy metals in water is described in Fig. 1.1.

Due to dietary intake, the human organism contains a certain amount of most of the heavy metals. They can enter the organism by food or beverages. According to WHO (2005), Ca, Na, K, Cl, Mg, Fe, Zn, Cu, Cr, I, Co, Mo, and Se have essential roles in human health. The elements B, Mn, Ni, Si, and V are second tier in their beneficial health effect and Pb, Cd, Hg, As, Al, Li, and Sn are toxic elements. Most of the elements cited can be delivered to humans via drinking water and food. The contribution of the elements from drinking water varies from 1% to 5%, depending on the element and water quality. In the case of Ca and Mg, the contribution from water can reach 20%. Obviously, the

Table 1.4 Committed Unit Doses ($\mathrm{mSv\,Bq^{-1}}$) of Four Key Isotopes, Uranium and Radium by Age Group

	Age Group (Year)					
Radionuclide	**<1**	**1–2**	**2–7**	**7–12**	**12–17**	**>17**
^{238}U	3.4×10^{-4}	1.2×10^{-4}	8.0×10^{-5}	6.8×10^{-5}	6.7×10^{-5}	4.5×10^{-5}
^{234}U	3.7×10^{-4}	1.0×10^{-4}	8.8×10^{-5}	7.4×10^{-5}	7.4×10^{-5}	4.9×10^{-5}
^{226}Ra	4.7×10^{-3}	9.6×10^{-4}	6.2×10^{-4}	8.0×10^{-4}	1.5×10^{-3}	2.8×10^{-4}
^{228}Ra	3.0×10^{-2}	5.7×10^{-3}	3.4×10^{-3}	3.9×10^{-3}	5.3×10^{-3}	6.9×10^{-4}

Based on IAEA, 1996. International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources. International Atomic Energy Association, Vienna.

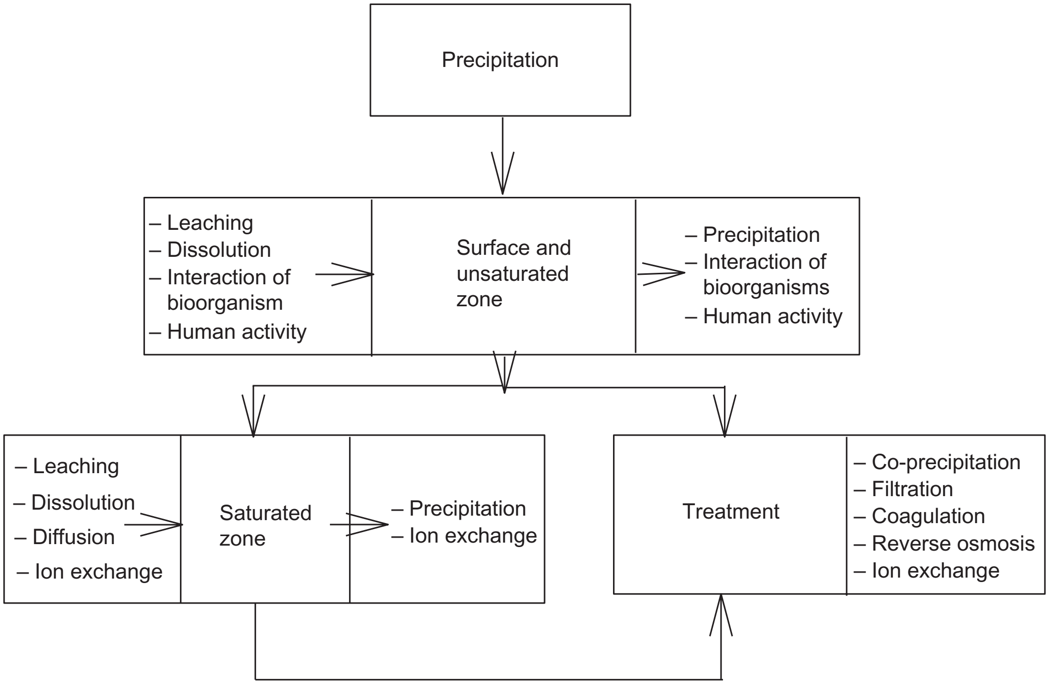

Fig. 1.1 Processes controlling the level of heavy metals in water.

contents of the essential and beneficial elements in drinking water are recommended by the relevant international organizations or follow national requirements.

The quality of natural water depends on its mineralization and chemical composition, which is controlled by the surrounding environment, hydrogeological and geological conditions, and civil culture. In developed countries, tap water usually has to conform to government regulations or WHO guidelines (WHO, 2005) and is delivered to the home by a network of water transport pipes. Many inhabitants living in industrial cities often purchase bottled or mineral waters. The criteria for quality with bottled water are much more lax than those for tap water. The mineralization and chemical composition of bottled water often displays a significantly wider range than that of tap water. The typical ranges of the total dissolved solids and the concentrations of most metals in uncontaminated surface, bottled mineral, and mineral waters are summarized in Table 1.5.

Generally, the concentrations of trace heavy elements (Mn, Ag, Al, Hg, Cd, etc.) in mineral water are comparable or significantly lower (especially the maximum values) than those in surface water. The phenomena can be connected with the fact that the surface water in contact with soil and weathered rocks usually contains a lot of

Table 1.5 Statistics on the Characteristic Concentrations (mg L^{-1}) of Principal and Trace Metals in Drinking Water Originating From Surface, Bottled Mineral, and Mineral Sources

	Uncontaminated Surface Water			Bottled Mineral Water			Mineral Water		
Element	**Min**	**Max**	**Average**	**Min**	**Max**	**Average**	**Min**	**Max**	**Average**
TDS	4	500	345	160	2930	970	150	3870	1850
Ca	1	200	88	28	548	149	54	730	288
Mg	0.1	64	10	7	130	40	18	196	72
Na	2	200	60	1	135	32	6	155	55
K	0.4	20	3.8	0.5	52	7.5	1.3	18.4	6.3
Fe	0.01	5	2.0	–	–	–	0.55	20.3	7.0
Ba	0.01	1	0.044	–	–	–	0.07	4.62	1.1
Mn	0.01	3	0.021	–	–	–	0.1	2.0	0.7
Ag	0.0001	0.031	0.0035	–	–	–	2×10^{-6}	8×10^{-4}	1.3×10^{-4}
Zn	0.002	0.2		–	–	–	0.001	0.127	0.021
Cu	0.001	0.2	0.0035	–	–	–	0.0008	0.107	0.008
Ni	0.005	0.1	0.013	–	–	–	2×10^{-5}	0.012	0.0044
Co	0.001	0.1	0.0017	–	–	–	0.0003	0.0025	0.0011
Pb	0.001	0.1	0.004	–	–	–	4×10^{-5}	0.0062	7×10^{-4}
Hg	0.00005	0.01	0.0007	–	–	–	1×10^{-5}	0.0008	1.5×10^{-4}
Cd	0.0001	0.2	0.0065	–	–	–	1×10^{-5}	1.9×10^{-4}	3.6×10^{-5}
Al	0.005	1	0.015	–	–	–	3×10^{-5}	0.06	0.0056
Cr	0.001	3.25	0.201	–	–	–	0.0016	0.0093	0.0042
Mo	0.001	0.2	0.018	–	–	–	1×10^{-5}	0.0011	0.0002
V	0.0001	0.04	0.002	–	–	–	17×10^{-5}	0.0021	0.00056
Zr				–	–	–	1×10^{-4}	0.0019	4×10^{-4}
As	0.002	0.05	0.005	–	–	–	3.1×10^{-4}	0.015	0.0021

Based on Dojlido, J., 1995. Chemistry of Surface Water. (Ekonomia i Środowisko); Chau, N.D., 2010. Natural Radioactivity of Selected Mineral Waters in the Polish Carpathians. JAK, Kraków, 206 p.

microbio-organisms undergoing degradation processes. The dissolved organic compounds and trace elements are absorbed by the rocks during the migration of deeply penetrating water. Due to the long-time retention of water in the rock formation, many interaction processes such as leaching of the minerals from the rocks, ion exchange and so on result in the total dissolved solids (TDS) and concentrations of major elements (Ca, Mg, Na, Fe) of the mineral and bottled mineral waters being high or even very high for groundwater occurring more than a few hundred metres deep.

Calcium

Calcium is one of the main elements of the rocks and soil, and it provides about 3.4% of the earth's crust. The principal calcium minerals are calcite $CaCO_3$, anorthite $CaAl_2Si_2O_8$, dolomite $CaMg(CO_2)_2$, gypsum $CaSO_4{\cdot}2H_2O$, anhydrite $CaSO_4$, fluorite CaF_2, fluorapatite $Ca_5(PO_4)_3F$, and hydroxyapatite $Ca_5(PO_4)_3OH$ (Bolewski and Manecki, 1993). The occurrence of Ca in water is mostly connected with leaching from the soil and rocks. In groundwater, Ca can be precipitated or dissolved in water depending on the physicochemical characteristics. Generally, Ca constitutes a main element in the mineral composition of the water (TDS). The concentration of calcium in mineral and drinking water varies from a dozen to a several hundred mg L^{-1} (Chiba et al., 2006). Calcium occurs in water basically as the ion Ca^{2+}; it can also be in complex forms such as: $[CaSO_4]$, $[CaCO_3]$, $[CaHCO_3]^+$, and $[CaOH]^-$. The maximum amount of Ca in water depends on the temperature and pressure; at 18°C and 1000 hPa the Ca content in water is no higher than 1 g L^{-1} (Jaworska-Szulc et al., 2017). Calcium is a principal element for humans and animals. Every adult should consume 1 g of Ca per day. According to the WHO (2017) guideline, the Ca content in drinking water should range from 50 to 200 mg L^{-3}. A deficiency of calcium can be a factor in heart problems and many diseases connected with the spine.

Magnesium

Magnesium is a principal element in the soil and rocks, and it makes up 1.9% of the earth's crust. The major magnesium-containing minerals are dolomite and magnesite $MgCO_3$. The occurrence of Mg in water depends on the host rock and the physical and chemical characteristics of water. In a similar manner to Ca, Mg is also the main component of the water TDS, in mineral and drinking water and the concentration of Mg ranges from several to 200 mg L^{-1}. Depending on the water mineralization, the Mg contribution ranges from nearly 10% up to 40% of mineralization composition. Apart from Mg^{2+} as a form in the water, Mg can occur in the forms of $[MgSO_4]^0$, $[MgCO_3]^0$, $[MgHCO_3]^+$, and $[MgOH]^+$ (Drever, 1997). The mass ratio Mg:Ca in drinking and mineral water varies from 1:4 to 1:2. Magnesium is a useful element for humans and animals and a shortage of magnesium can lead to cancer. There are no limits for magnesium in drinking water except in relation to hardness. According to the WHO guidelines (WHO, 2017), the concentration of Mg should be 50 mg L^{-1}.

Sodium

Sodium is a main element in the soil and rocks and makes up 2.6% of the earth's crust. The Na concentration in mineral and drinking water depends on the water-bearing formation and hydrochemical type of water, and varies from a few mg L^{-3} to several hundred mg L^{-3}. Sodium in groundwater is mainly due to leaching from the soil and rock and ion exchange, the last process often appearing in groundwater hosted in the deep reservoir. The main form of occurrence is Na^+, but in cases of high mineralization sodium can occur in $[NaSO_4]^-$, $[NaCO_3]^-$, and $[NaHCO_3]^0$ complexes (Dojlido, 1995). The complex fraction of sodium in water of low mineralization is below 5%. Sodium is very useful for humans and every adult consumes from 4 to 24 g daily. However, high Na concentration is very dangerous, especially for children, and the sodium concentration in drinking water should not be higher than 200 mg L^{-1} (WHO, 2005).

Potassium

Potassium makes up 2.4% of the earth's crust. Leucite $KAlSi_2O_6$, sylvine KCl, and carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ are major potassium minerals that are resistant to leaching processes. The majority of potassium ions in the environment are absorbed by the biosystem. In consequence, the potassium concentration in water is far lower than the sodium one by a factor of 4–10 and the concentration ranges from a fraction of a milligram to tens of mg L^{-1} (Macioszczyk and Dobrzyński, 2003). Similarly to sodium, potassium occurs in the K^+ form in water, but in cases of high mineralization potassium can be found in $[KCO_3]^-$ and $[KHCO_3]^0$ complexes. There is no limit to potassium content in drinking water. Deficiency of potassium can lead to giddiness (WHO, 2017).

Iron

Iron makes up 5.6% of the earth's crust. There are many minerals containing Fe, but the principal minerals including this element can be noted as hematite Fe_2O_3, magnetite Fe_3O_4, limonite $Fe(OH)_3$, siderite $FeCO_3$, and pyrite FeS_2 (Bolewski and Manecki, 1993). The background process leading to the presence of Fe in natural water is leaching from rock formation. Generally, the Fe content in drinking and mineral water varies from 0.01 to 20 mg L^{-1}. The quantity of Fe in groundwater increases with the depth of the aquifer formation (Fig. 1.2). In nature, iron occurs in compounds where iron is composed of Fe^{2+}, $[FeOH]^+$ and $[Fe(OH)_3]^-$, or Fe^{3+}, $[Fe(OH)]^{2+}$ and $[Fe(OH)_2]^+$ (Dojlido, 1995; Macioszczyk and Dobrzyński, 2003). The forms of occurrence and contribution of each complex is related to the water Eh and pH. In water with a pH higher than 7, iron chiefly

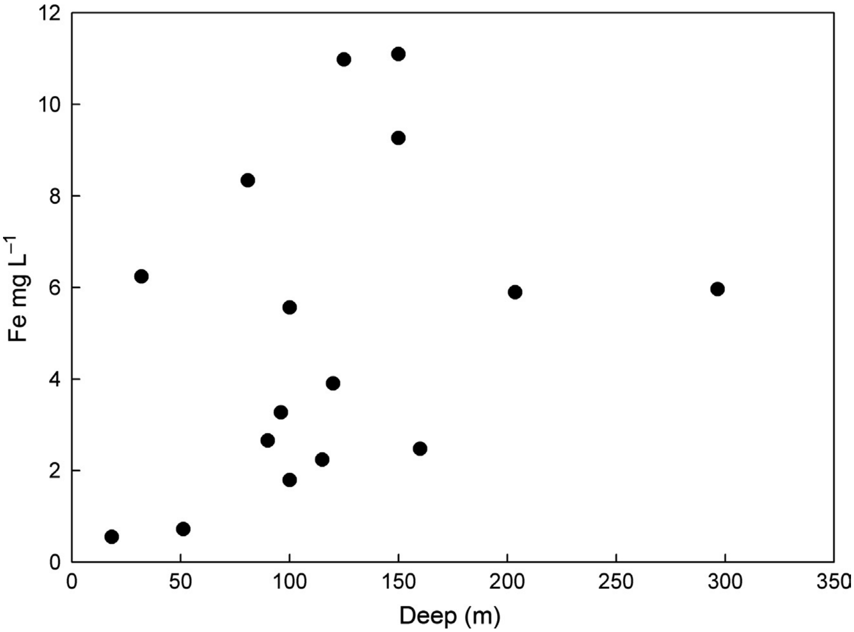

Fig. 1.2 Relationship between Fe concentrations in Ca-Mg-HCO_3 mineral waters and in deep water-bearing formations (Chau, 2010).

occurs as $[Fe(OH)_2]^+$. Ferrous complexes, where Fe occurs as Fe^{2+}, are often present in anaerobic water where they dominate under reducing conditions. Such conditions are often observed in groundwater occurring at great depth. If water with ferrous complexes is exposed to the atmosphere, the ferrous complexes react with oxygen and ferric compounds are formed, which give an objectionable reddish-brown color to the water. Apart from the ion forms, iron can be found in colloids. Colloid forms are often seen in surface water or in tap water originating from surface reservoirs. Fe deficiency is often observed in people suffering from diseases of the blood system.

Barium

There is no barium in the pure form in the environment; barite $BaSO_4$ and withrite $BaCO_3$ are the major barium minerals. Barium is a common component of water mineralization, but its concentration in drinking and mineral water is low enough and varies from 0.01 to 4 mg L^{-1}. Such low concentrations are related to the high resistance of barium minerals to weathering and leaching. In water of low and medium mineralization, barium chiefly occurs in the ion form (Ba^{2+}). Barium is generally a harmful element for the organism; therefore, the recommended barium concentration in mineral and drinking water is lower than 1.0 mg L^{-1} (WHO, 2017).

Manganese

Manganese is a ubiquitous element in soil and sediment; its constitutes 0.08% of the earth's crust and occurs as pyrolusite MnO_2 and braunite Mn_2O_3. In the environment, manganese can appear in compounds where Mn can be at valences of 2+, 3+, 4+, 6+, and 7+. Manganese oxides are extremely fine-grained with surface areas of around $200\,m^2\,g^{-1}$. Due to their properties, manganese oxides have very high adsorption ability for heavy elements. The occurrence of Mn in water is chiefly connected with leaching processes; its concentration in water ranges from 0.1 to $3\,mg\,L^{-1}$. The 2+ valence forms: Mn^{2+}, $[MnOH]^+$, $[Mn(OH)_3]^-$, $[MnSO_4]^0$, and $[MnHCO_3]^+$ are not stable. In chloride water or in water of $pH < 6$, manganese can appear as chloride compounds $[MnCl]^+$, $[MnCl_2]^0$, and $[MnCl_3]^-$. In water rich in SO_4 or $[HCO_3]^-$, Mn can occur as $[MnSO_4]^0$ and $[MnHCO_3]^-$. Under strongly reducing conditions, Mn can migrate from the sediment into the water. Referring to the WHO guidelines, the maximum acceptable concentration of Mn in drinking water amounts to $0.1\,mg\,L^{-1}$ (WHO, 2017). High manganese concentrations can lead to a black precipitate coating the pipes and may cause an undesirable taste. High content of manganese in water can act as a poison, and the limit of Mn in drinking water should not exceed $50\ \mu g\ L^{-1}$ (RMZ, 2017). However, a systematic deficiency of Mn in organisms can lead to chlorosis.

Silver

Naturally, silver mostly occurs as silver sulfite Ag_2S, and partly as pure metal or oxide (Ag_2O), chloride ($AgCl$), and fluoride (AgF) (Bolewski and Manecki, 1993). Silver and its compounds are insoluble and immobile in the environment. The permissible silver concentration in tap water for disinfection is $50\,\mu g\,L^{-1}$. Generally, the Ag concentration in surface and underground waters varies from zero to a few tens of $\mu g\,L^{-1}$. Water with high enough Ag content ($\geq 0.5\,mg\,L^{-1}$) can become a factor leading to argyria. The permissible level of Ag in drinking water is lower than $50\,\mu g\,L^{-1}$ (WHO, 2017).

Copper

Copper is widespread in the environment; there are many Cu minerals: chalcopyrite ($CuFeS_2$), cuprite (Cu_2O), malachite $[Cu(OH)_2{\cdot}CuCO_3]$, and bornite (Cu_5FeS_4). Copper is soluble in water at low pH; under alkaline conditions its solubility is limited. Copper can occur with valences of +1, +2, and +3, but the most popular is in compounds with Cu at +2. In water, copper occurs as the ion Cu^{2+} and as complexes $[CuOH]^+$, $[CuCO_3]^0$, and $[Cu(OH)_4]^{2-}$. In water rich in organic matter, Cu often binds to it (Drever, 1997). The Cu present in water is principally caused by the leaching of malachite or copper hydroxide in an acid or basic environment, respectively (Dojlido, 1995). The Cu concentration varies from 1 to above 100 μg L^{-1}. The permissible copper concentration in drinking water is 1 mg L^{-1}. Copper is an essential element for human life, but an enhanced content of this metal can cause people to suffer from anemia, and liver and kidney damage (Salem et al., 2000). Copper in large doses is harmful to people with certain disorders.

Nickel

Nickel provides a 0.01% contribution to the earth's crust. The main nickel minerals are pentlandite $(FeNi)_9S_8$, millerite NiS, and garnierite $(NiMg)_6Si_4O_{10}(OH)_8$. Nickel occurs at various valences from −1 to +4; however, the most popular is the form of +2 (Ni^{2+}) (Dojlido, 1995). In water, nickel often binds with chloride, or sulfurous or phosphorous-creating ligands. In drinking and mineral waters, nickel concentration ranges from 2×10^{-5} to 0.015 mg L^{-1}. Surface water is easily contaminated by Ni from diesel cars [in some places that is, River Ganges, water nickel can rise to above 1.2 mg L^{-1} (Dipak, 2017)] and ore exploitation (Pham et al., 2017). The permissible Ni concentration in drinking water is 0.07 mg L^{-1}. High Ni content in water can be harmful to people, especially for expectant mothers (Salem et al., 2000).

Cobalt

Cobalt usually occurs in the form of sulfite or with arsenic. Cobalt minerals are cobaltite CoAsS, linnaeite Co_3S_4, smaltite (Co,Ni)As, and carrolite $CuCo_2S_4$. Cobalt can have a valence from −1 to +4, but in water it appears as the ion Co^{2+}. In anthropogenically contaminated water, Co can bind with cyanide or ammonia as $K_4[Co(CN)_6]$ and $K_3[Co(NH_3)_6]$ complexes (Dojlido, 1995). In mineral and drinking water, Co content is low and varies around 0.05 μg L^{-1}. Cobalt is needed at a low level, but can be hazardous at high concentrations in water (WHO, 2017).

Lead and Cadmium

Lead and cadmium possess some common characteristics; they predominantly occur in water at a valency of +2 (free or complexes). Their solubility in water increases with lowering of the pH. In alkaline water, they can be precipitated as hydroxide, carbonate, or sulfite forms. There are many lead minerals, but galena PbS, anglesite ($PbSO_4$), and cerrusite $PbCO_3$ are the major ones. In water, lead can occur as Pb^{2+} and $[PbCO_3]^0$. In neutral water, the contributions of the occurrence of forms of Pb^{2+} and $[PbOH]^+$ are comparable; in alkaline water (pH >8), Pb can complex with chlorine or sulfate. Lead can migrate into water as a consequence of human activity, that is, before the year 1990 most water pipes were made of lead, and the concentration of Pb in tap water varied from 50 to 100 $\mu g\,L^{-1}$. After the replacement of lead pipes by copper or plastic ones, the average Pb content in tap water was lowered to 3 $\mu g\,L^{-1}$. Generally, the concentration of lead in ground waters is around 5 $\mu g\,L^{-1}$; higher Pb concentrations can be observed in wells and shallow water resources located near Pb-Zn deposits, motorways, or in rural towns with a large residential density. The permissible lead concentration in drinking water is lower than 10 $\mu g\,L^{-1}$. Lead is a harmful element even at low concentrations and can be removed from the human body in urine, but it is very dangerous for children since this metal can accumulate in the lungs, kidneys, and liver. Following exposure to lead for period of a few months or years, children can suffer many metabolic illnesses such as effects on the nervous system, high blood pressure, slow growth, and renal failure (Groopman et al., 1985).

Cadmium in the lithosphere mostly occurs in CdS or $CdCO_3$ compounds, while in water this metal can be seen as free Cd^{2+} ions or: $[CdCO_3]^0$, $[CdSO_4]^0$, and $[CdCl]^-$ complexes. In surface water, cadmium can attach to suspended particles. In uncontaminated drinking and mineral water, the cadmium concentration is from ≤1 to a few $\mu g\,L^{-1}$. Cadmium can be disseminated in the environment from paint and pigments, mining, the burning of coal, and smelting plants. This element may enter drinking water as a result of the corrosion of galvanized pipes (Salem et al., 2000; Cheng, 2003; Rosborg, 2005; Dipak, 2017). Generally, cadmium is regarded as a carcinogenic element; it remains in the body for a long time and accumulates in the kidney and liver. Cd can replace Ca in bone, leading to painful bone disorders. The level of 3 $\mu g\,L^{-1}$ is the maximum permissible Pb concentration in drinking water (WHO, 2017).

Mercury

Mercury is a metallic element occurring in the liquid phase at room temperature. In nature, mercury can partly sublimate from the liquid phase into the vapor one. In the vapor phase, mercury occurs as a single atom and does not undergo oxidization. Mercury vapor is very toxic. In the environment, mercury can be found as free atoms or in its sulfide compound (HgS). In regions where there are Hg deposits or an active volcano or forest fire, there is a significantly higher concentration of mercury in the atmosphere. The presence of Hg in water mostly originates from rain or snow. In uncontaminated regions, the Hg concentration in water is very low and ranges around $n \times 10^{-4}\,mg\,L^{-1}$. Mercury in water occurs in the soluble form as Hg^{2+}, $Hg_2{}^{2+}$, and Hg^0 or in complexes such as $[HgOH]^+$, $[HgCl]^+$, $[HgCl_2]^0$, $[HgCl_3]^-$, $[HgCl_4]^{2-}$, and $[HgS_2]^{2-}$. The form of occurrence is determined by the conditions prevailing in the water; for example, in water with a redox potential

$Eh \geq 500$ mV, mercury occurs in complexes, while under reducing conditions it can exist as the free element, and in water rich in sulfur mercury can precipitate as HgS. In surface water, mercury mostly binds with organic ligands in the suspended materials such as CH_3Hg^+, $C_2H_5Hg^+$, or $C_6H_5Hg^+$; the contribution of Hg in the suspended form is often 5- to 25-fold higher than those of the single ion (Hg^{2+}) or free atom Hg^0 (Dojlido, 1995). Mercury is classified as the most toxic element. The element accumulates in the kidneys and causes some benign tumors. The permissible level of Hg in drinking water is below 0.5 $\mu g\ L^{-1}$ (Kumar and Puri, 2012; RMZ, 2017).

Aluminum

Aluminum is the third most abundant element, contributing about 8% to the earth's crust. Its principal minerals are gibbsite $Al(OH)_3$ and bauxite $Al_2O_3 \cdot 2H_2O$. In water, aluminum complexes strongly with sulfate or fluoride in forms such as $[Al(SO_4)]^+$ and $[Al(SO_4)_2]^-$ or $[AlF]^{2+}$ or $[Al(H_2O)_6]^{3+}$ with no free aluminum ion Al^{3+}. The form of occurrence of Al is related to the pH; at $pH \leq 4$ $[Al(H_2O)_6]^{3+}$ is dominant, but at $pH \geq 8$ the $[Al(OH)_4(H_2O)_2]^-$ form prevails (Dojlido, 1995). Due to the low solubility of aluminum compounds, the concentration of Al in water is very low and varies from $n \times 10^{-5}\ mg\ L^{-1}$ to near $0.1\ mg\ L^{-1}$. An additional source of Al in drinking water is the use of aluminum salts as coagulants in drinking-water treatment to reduce organic matter content, turbidity, and levels of microorganisms. Aluminum is not an essential element for human life; the presence of redundant amounts of this element in the body is believed to lead to Alzheimer's disease, but this statement is currently under discussion (WHO, 2005). The permissible concentration of aluminum in drinking water is $1\ mg\ L^{-1}$ (RMZ, 2017).

Arsenic

Arsenic is an element that is toxic to humans; the degree of hazard of As depends on its complexes. Compounds of As^{3+} are more toxic than As^{5+} ones, the most hazardous being AsH_3. In some Asian countries where the arsenic concentration in surface water is high (above $2\ mg\ L^{-1}$), many people suffer from peripheral neuropathy, skin cancer, bladder and lung cancers, and peripheral vascular disease, which have been observed in populations ingesting arsenic-contaminated drinking water. Due to the presence of five electrons in the outer orbital, arsenic can occur with valences from −3 to +5, but in water compounds in which it is at +5, +3, 0, and −3 are often observed. The form of occurrence is mostly controlled by redox potential and the level of pH. Under reducing conditions ($Eh < 0$), the form +3 is dominant. When water is rich in sulfur, As precipitates as a sulfide; if sulfur is absent As remains in water in the form of arsenic acid (H_3AsO_3). Under oxidizing conditions ($Eh > 0$), forms with As^{5+} are in the majority; at pH values from 2 to 6 As occurs as the $H_2AsO_4^-$ ion and at pH values from 7 to 10 as $HAsO_4^{2-}$ (Drever, 1997). The arsenic concentration in uncontaminated drinking water varies from nil to 0.015 mg L^{-1}. The As concentration reaches 0.85 mg L^{-1} in tap waters in some provinces in China and Bangladesh (Cheng, 2003) due to industrial development. The principal source of arsenic in the environment is the burning of coal and oil and ore smelting although As can enter the environment by leaching from rocks or from the materials ejected from an active volcano. The maximum permissible concentration of arsenic is 0.01 mg L^{-1} (WHO, 2005).

Chromium

Chromium is widely distributed in soil and rock, and makes up 0.037% of the earth's crust. The major chromium mineral is chromite ($FeCr_2O_4$). Under oxidizing conditions, chromium occurs at a valence of +6 in water; at pH <6 the ion $HCrO_4^-$ is dominant and at pH > 7 the CrO_4^{2-} form is most abundant. Under intermediate and reducing conditions, chromium appears at a valence of +3 and mostly in forms of chromium oxide (Cr_2O_3). The main source of distribution of chromium in the environment is the burning of fuel (coal, oil). The average concentration of Cr in water is nearly 5 µg L^{-1}. In some contaminated surface waters, the Cr concentration can reach a few hundred µg L^{-1} (Salem et al., 2000; Paul and Sinha, 2013). Chromium is essential for the ecosystem (vegetable, animal, and human) in low quantities, while in large quantities it becomes a toxic substance, especially in the form Cr^{6+}. Long exposure can cause kidney and liver disease and damage to the nerves and the circulatory system. The maximum permissible concentration of chromium in drinking water is 50 µg L^{-1}.

Molybdenum

In the natural environment, molybdenum often occurs as molybdenite (MoS_2) or wulfenite $PbMoO_4$. The concentration of molybdenum in water is usually lower than 0.02 mg L^{-1}. Molybdenum can occur in compounds where it has a valence of +2, +3, +5, and + 6, but the forms with a valence of +6 are the most stable and the forms that are the most abundant in water. The main sources delivering molybdenum to water are opencast uranium-molybdenum, iron and coal mines, or large industrial plants (Migaszewski and Gałuszka, 1998). Molybdenum is considered as an essential element and the daily dietary requirement is 0.2 to 0.3 g for an adult. An excess of this metal in the organism can cause bone deformation or slower physical development and more growth abnormalities. Salem et al. (2000) reported there is a relationship between molybdenum contamination in drinking water and patients suffering from cirrhosis. The recommended permissible limit of molybdenum is 70 μg L^{-1} for drinking water (WHO, 2017).

Vanadium

Vanadium comprises 0.018% of the earth's crust, and vanadium is found as the minerals patronite (V_2S_5) and vanadinite $Pb_5V_3O_{12}Cl$. Coal-fired electric power stations can be major sources of vanadium in the environment. The concentration of vanadium in water is lower than 20 μg L^{-1} (Dojlido, 1995). A low level of vanadium is essential for the organism to prevent heart disease, while an excess of this element in the human body can cause stomach ache or diseases connected with the respiratory system.

1.2.2.2 Radioactive Elements (Radionuclides)

Apart from the above-mentioned chemical elements, radioactive elements also occur in water. The concentration of radionuclides in water is usually low, but in some cases the risk they pose to human health can be observed. Radionuclides in the environment can be divided into three groups on the basis of their origin: (i) cosmogenic, (ii) geogenic, and (iii) anthropogenic radionuclides. Cosmogenic radionuclides are produced in the atmosphere as a consequence of the interaction of primary and secondary cosmic radiation with components of the air. This group contains over 20 radioisotopes from tritium to krypton and including the cosmic radiation comprises nearly 10% of the total dose from natural radiation sources. The cosmogenic radionuclide most relevant to public exposure is ^{14}C, which is a constant rate product of the interaction of slow neutrons with ^{14}N in the atmosphere and contributes about 12 μSv to the annual average dose rate (UNCEAR, 2008).

Anthropogenic radionuclides are defined as those radioisotopes generated from man-made sources. The radionuclides are released from nuclear power plants, nuclear accidents, nuclear tests, or scientific and medical institutes using nuclear materials. The major radioisotopes belonging to this group are ^{90}Sr, ^{95}Zr, ^{134}Cs, ^{137}Cs, ^{131}I, isotopes of plutonium (^{239}Pu, ^{240}Pu, ^{241}Pu), and ^{3}H, and ^{14}C. Before 1945, excluding tritium and radiocarbon (^{14}C) that are constantly generated in part by cosmic radiation, the presence of all man-made isotopes was not observed. During the nuclear testing period (1945–80), the annual committed dose rate increased and reached a maximum of 110 μSv in 1963 and decreased to 5 μSv in 1980.

Although cosmogenic and anthropogenic radionuclides contribute a certain level of committed dose rate to the environment, in the hydrosphere, and especially in natural water used as a beverage, the concentrations of radionuclides usually are at a level at which the annual committed dose rate resulting from consumption pathways is very low; so, both cosmogenic and anthropogenic radioisotopes are omitted and not considered in this chapter.

The geogenic group contains radionuclides present in the earth's crust since its formation. Their half-life periods ($T_{1/2}$) are longer or comparable with the age of the Solar system that is, ^{40}K ($T_{1/2} = 1.3 \times 10^{10}$ year), ^{87}Rb ($T_{1/2} = 4.8 \times 10^{10}$ year), and radionuclides belonging to three series with primordial isotopes ^{238}U ($T_{1/2} = 4.5 \times 10^{9}$ year), ^{232}Th ($T_{1/2} = 1.39 \times 10^{10}$ year), and ^{235}U ($T_{1/2} = 7.13 \times 10^{8}$ year). The isotopes of the decay series undergo successive nuclear transformations with the emission of alpha or beta and gamma radiation until they form stable lead isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb).

Geogenic radionuclides are ubiquitous in all spheres and environmental material. They contribute over 83% of the total average annual committed dose rate received by the population on the Earth (UNCEAR, 2000).

From the distribution viewpoint, geogenic radionuclides can be classified into two groups: (i) naturally occurring radioactive materials (NORM) and (ii) technologically enhanced naturally occurring radioactive materials (TENORM). The distribution of the radioactive elements of the first group in the environment is not affected by human activities, while the second group is composed of materials that contain elevated levels of natural radionuclides resulting from human activities (mining, melting, agricultural fertilizer, fuel combustion, and so on).

Generally, both the radioactivity level and the concentration of the individual natural radionuclides depend on the geological water-bearing formation in the region. Table 1.6 shows the concentration ranges of ^{238}U, ^{226}Ra, ^{228}Ra, ^{222}Rn, ^{210}Pb, ^{210}Po, and ^{40}K in groundwater occurring in various types of host rock.

The contents of natural radionuclides in groundwater vary over a very broad range; for granite and sandstone aquifers, the concentration of uranium and radium can vary from a fraction of $\mathrm{mBq\,L^{-1}}$ to several tens of $\mathrm{Bq\,L^{-1}}$. In general, the concentration of the natural radionuclides in groundwater is controlled by the lithology of the water-bearing formation, pH, Eh, temperature, water mineralization and its chemical composition, and the retention time of the water in the rock formation. People often consume bottled mineral water or spring artesian water and the TDS of drinking water usually does not exceed $3000\,\mathrm{mg\,L^{-1}}$. The concentrations of ^{238}U, ^{234}U, ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{210}Po in bottled mineral and artesian water are summarized in Table 1.7.

Table 1.6 Ranges of Concentration of Selected Radionuclides in Groundwater Occurring in Various Types of Host Formation (Chau et al., 2011)

Water Host Formation	^{238}U (mBql^{-1})	^{226}Ra (mBql^{-1})	^{228}Ra (mBql^{-1})	^{222}Rn (Bql^{-1})	^{210}Pb (mBql^{-1})	^{210}Po (mBql^{-1})	^{40}K (mBql^{-1})
Granite (Andrews et al., 1989; Salih et al., 2002)	0–5300	0–6500	0–1620	n.10–n.10^5	0–430	0–656	–
Granite/basalt (Vinson et al., 2008; Seiler, 2011)	7.4–3700	37–148	–	–	0–160	0.37–6590	11–37,000
Granite/black shale (Lee et al., 2001)	6.7–3300	–	–	–	–	–	–
Metamorphic rocks (King et al., 1982; Almeida et al., 2004)	0.1–80	0.7–962	1.1–1500	–	–	–	–
Sandstone/limestone/shales (King et al., 1982; Bonotto and Bueno, 2008; Chau 2010)	0.26–18,500	1.1–1490	0.73–877	–	0–288	–	14–10,240
Sand (Tricca et al., 2001; Jobbagy et al., 2010)	0.04–22.2	0.4–1.1	0.08–333	–	–	–	–
Limestone (Dabous, 1994)	0.014–0.132	–	–	–	–	–	–
Phosphate rocks (Minster et al., 2004)	1.44–138	74–30,800	–	–	–	–	–

Table 1.7 Ranges of Concentration of Selected Radionuclides in Mineral and Drinking Waters in Several Countries (Chau et al., 2011)

Country (Samples) (Reference)	^{238}U (mBql^{-1})	^{234}U (mBql^{-1})	^{226}Ra (mBql^{-1})	^{228}Ra (mBql^{-1})	^{210}Pb (mBql^{-1})	^{210}Po (mBql^{-1})	^{40}K (mBql^{-1})
Austria (58) (Wallner et al. 2008; Wallner and Steininger, 2006)	1÷73.6	1.4÷79	0.6÷211	5.3÷236	≤3÷17	0.4÷6.1	–
Belarus (19) (Ushko and Chau, 2014)	22.7÷93.8	18.5÷289	<5÷622	<10÷2,080	–	–	–
Finland (176) (Vesterbacka et al., 2006)	–	–	<10÷1,300	<20÷317	–	–	–
Germany (192) (Gans et al., 1987)	–	–	<5 ÷6,290	<10÷40	–	–	–
Poland (Chau, 2010)	0.6÷19.2	1.7÷74.7	0.8÷525	10÷393	–	–	15÷10,064
Spain (24) (Bayés et al., 1996)	–	–	15÷2,570	10÷2,440	–	–	–
Sweden (328) (Salih et al., 2002)	–	–	<5÷4,900	<10÷1,600	–	–	–
Switzerland (402) (Deflorin and Surbeck, 2003)	–	–	–	<10÷400	–	–	–
Brasil (34) (Godoy et al., 2001)	–	–	2÷220	<10÷1,020	10÷510	–	–
China (428) (Zhuo et al., 2001)	–	–	<5÷940	<10÷490	–	–	–

Potassium ^{40}K

There are three isotopes of potassium, ^{39}K, ^{40}K, and ^{41}K, with abundances of 93.0782%, 0.0118%, and 6.91%, respectively. The isotope ^{40}K is radioactive and undergoes two alternative decays: (i) beta decay to ^{40}Ca (88.8%) with $T_{1/2}=1.49\times10^9$ year and (ii) electron capture (11.2%) to ^{40}Ar with $T_{1/2}=1.19\times10^{10}$ year and emission of γ radiation ($E_\gamma=$ 1460 keV). The level of ^{40}K activity in water can be calculated taking into account its abundance in natural potassium and the content of this element in the water studied (Chau, 2010; Kozłowska, 2009). The permissible limit for potassium is 12 mg L^{-1} and the maximum level of activity of ^{40}K in drinking water is 360 mBq L^{-1}.

Uranium

The average concentration of uranium in the earth's crust is equal to 3.5 ppm. The major uranium minerals are uraninite UO_2, autunite $Ca[UO_2|PO_4]_2 \cdot 10H_2O$, ianthinite $[UO_2][OH]_2$, uranospilite $Na_2[UO_2|AsO_4]_2 \cdot nH_2O$, and schröeckingeryte $NaCa_3[UO_2][F|SO_4][(CO_3)_3] \cdot 10H_2O$. Uranium occurs in the +2, +3, +4, +5, or + 6 valence states, but most commonly in the hexavalent form. In nature, uranium is commonly bonded with oxygen as a uranyl ion UO_2^{2+}. There are three natural uranium isotopes: ^{238}U, ^{235}U, and ^{234}U, with abundances of 99.28%, 0.71%, and 0.0057%, respectively. All uranium isotopes undergo α-decay. A quantity of 1 μg of natural uranium has an activity 25 mBq. Uranium is ubiquitous in nature. In general, the amount of uranium in igneous rocks is higher than that in sedimentary rocks. Acidic rocks contain higher quantities of uranium than basic and ultrabasic rock. The content of uranium in sandstone and limestone mainly depends on the shale content in the rocks (Bała, 2010). The uranium present in water results from leaching from rocks, natural deposits, the combustion of coal and other fuels, the use of fertilizers in agriculture, or the use of depleted uranium ammunition (Vidic et al., 2013; Lowson and McIntyre, 2013; Alvarado et al., 2014; Bister et al., 2015; Liu et al., 2017). Phosphate fertilizers often contain uranium >90 mgkg^{-1} (Pfister et al., 1976). Uranium from the spreading of fertilizers in fields can be dissolved in rainfall and migrate to surface and groundwater. The form of uranium complexes in water depends on the pH, the oxidation and reduction state, as well as on the amounts of anions, CO_2, phosphate, sulfate, and fluorite complexes. Under reducing conditions, U(IV) is dominant at pH levels below 8, while under oxidizing conditions U(VI) prevails at pH levels higher than 4 (Langmuir, 1978; Chau et al., 2011). In CO_2-rich water, the complex ions $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ prevail (Michard et al., 1987). In the presence of sulfate or fluorite UO_2^{2+}, UO_2F^+, and $UO_2SO_4^0$ forms dominate at pH levels below 4 (Drever, 1997).

The concentration of uranium in drinking water usually ranges from a few to several tens of mBq L^{-1} (Chau, 2010) excluding in some anomalous places where the uranium concentration in well water can reach 700 or 2020 μg L^{-1}. Due to the recoil effect, the ratio of the activity concentration of ^{234}U to that of ^{238}U ($^{234}U/^{238}U$) is often higher than 1 and decreases with increasing proportions of ^{238}U (Osmond and Cowart, 1976; Reynold et al., 2003; Chau and Michalec, 2009; Guerrero et al., 2016).

Fig. 1.3 shows the relationship between the uranium activity ratio ($^{234}U/^{238}U$) and the ^{238}U concentration detected in mineral water hosted in the Ojo Alamo aquifers in northwest New Mexico, United States, and in the Carpathian Flysch formations in south Poland. Both aquifers are mainly built up from sandstone and conglomerates.

Generally, the uranium concentration in mineral waters from both aquifers is below the maximum permissible value [15 μg L^{-1} = 180 mBq L^{-1} (^{238}U) recommended by the WHO (2005) and $^{234}U/^{238}U$ is higher than 2 for most waters having a ^{238}U activity below 4 mBq L^{-1}. Due to the mass ratio of $^{235}U/^{238}U$ being stable and equal to 0.007 in all natural environmental material, ^{235}U and its progeny are not concerned in hydrogeology and natural water used as a beverage. Due to the redox potential, the uranium concentration in groundwater decreases with the depth of the water-bearing formation (Fig. 1.4).

Uranium is a heavy and radioactive element, which may have a dual effect if it accumulates in humans. The chemical toxicity is a major

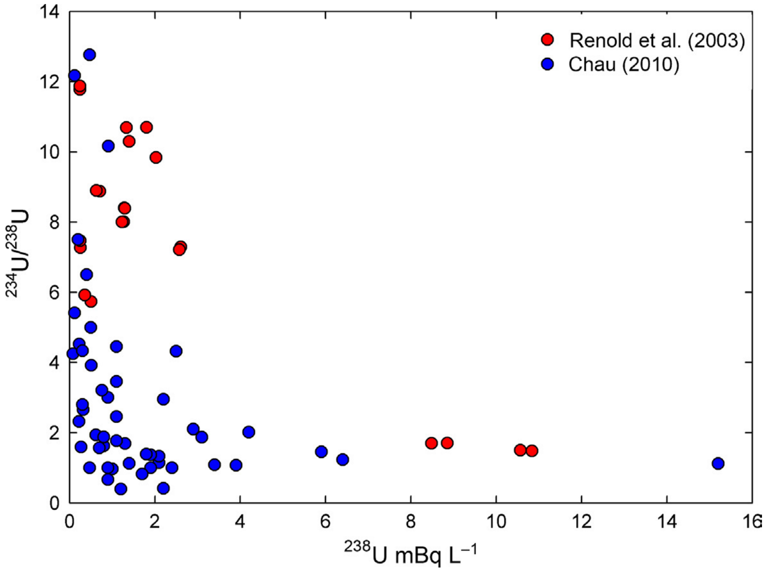

Fig. 1.3 Relationship between $^{234}U/^{238}U$ and ^{238}U concentration in mineral waters from Ojo Alamo and in Polish Carpathian aquifers.

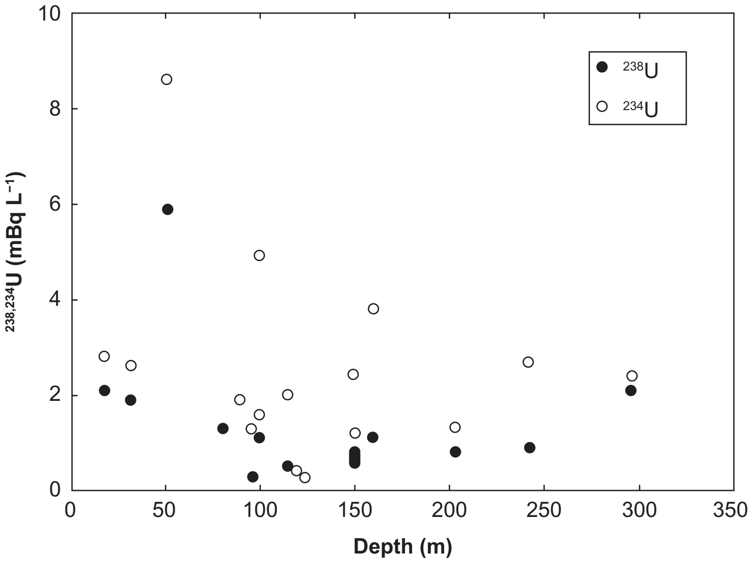

Fig. 1.4 ^{238}U and ^{234}U concentration in groundwater versus depth of water-bearing formation (Chau, 2010).

hazard to the kidneys, while radiotoxicity also arises from the irradiation of the bone surface and red bone. The linear correlation between the uranium content in the bones of people from Canada and the uranium concentration in drinking water was observed by Larivière et al. (2013). Malatova et al. (2016) noted the elevated concentration in the urine of miners and people working at the plants processing uranium ores in the Czech Republic.

Radium Isotopes

Radium belongs to the group of alkaline earth elements, and it always occurs in the 2+ valence state. Its chemical properties are similar to those of barium, calcium, and strontium and it generally forms insoluble sulfate and carbonate salts. Solubility decreases in the order $Ca^{2+} > Sr^{2+} > Pb^{2+} > Ba^{2+} > Ra^{2+}$. The chloride, bromide, nitrate, and hydroxide salts of radium are soluble in water. There are four radioactive isotopes in nature: ^{226}Ra with $T_{1/2} = 1620$ year that belongs to the ^{238}U decay series, ^{228}Ra ($T_{1/2} = 5.75$ year) and ^{224}Ra ($T_{1/2} = 3.64$ days) being the decay products of the ^{232}Th decay series, and ^{223}Ra with $T_{1/2} = 11.4$ days belonging to the ^{235}U decay series. The ^{223}Ra, ^{224}Ra, and ^{236}Ra isotopes are alpha decay isotopes while ^{228}Ra is a beta decay one. Generally, two isotopes ^{226}Ra and ^{228}Ra are of importance in drinking water. Although the $T_{1/2}$ of ^{224}Ra is short, its activity concentration in mineral water is comparable with that of ^{228}Ra and ^{226}Ra (Chau et al., 2017); so, in some circumstances ^{224}Ra should be studied, especially in mineral water served for direct consumption. By contrast, ^{223}Ra is not relevant as far as the ^{235}U question mentioned above (see the section on uranium) is concerned.

The occurrence of radium in water is governed by three major processes: (i) leaching from host rocks, (ii) sorption/desorption phenomena controlled by the physicochemical properties of water, and (iii) the alpha recoil effect. According to the processes mentioned in groundwater, the contents of ^{226}Ra and ^{228}Ra should reflect the contents of ^{238}U and ^{232}Th in the host rock formation to some degree (King et al., 1982; Sturchio et al., 1992). The radium content in water hosted in weathered intrusions and sandstone mixed with shale formations is often high and in some cases reaches a dozen Bq L^{-1} (Andrews et al., 1989; Bonotto, 2005; Chau et al., 2012; Walencik-Łata et al., 2016). By contrast, in aquifers hosted in sediments of marine origin (limestone, dolomite), very low radium contents were observed in water (Chau et al., 2009). Generally, the concentration of radium isotopes in water hosted in a pure sandstone formation is low and increases with admixtures of shale.

Fig. 1.5 shows the relationship between ^{226}Ra and ^{228}Ra contents in various types of groundwater from Poland, Spain, Austria, and Sweden (Salih et al., 2002; Chau, 2010; Wallner and Jabbar, 2010; Moron et al., 1986). The range of concentration of both isotopes is wide; there is an apparent relationship between the measured concentrations of ^{226}Ra and ^{228}Ra with a clustering of points around the $y = x$ line. However, in

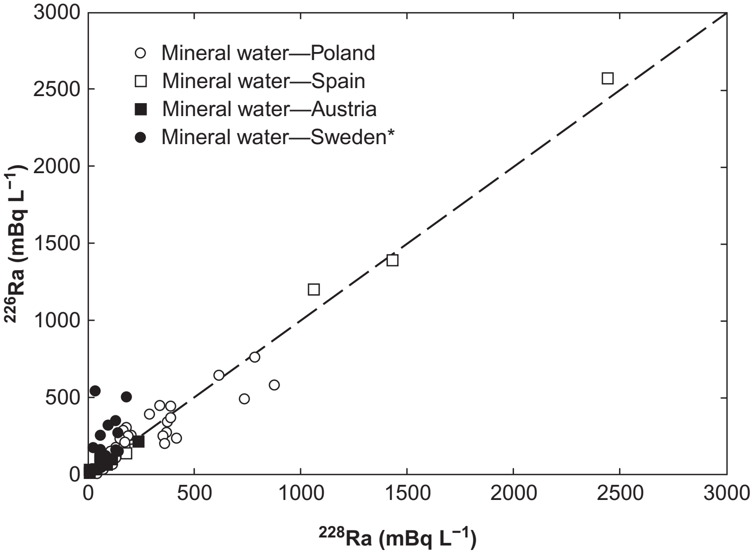

Fig. 1.5 Relationship between ^{228}Ra and ^{226}Ra activity level in selected groundwater systems in Europe (Salih et al., 2002; Chau, 2010; Wallner et al., 2007; Moron et al., 1986).

water in the Stripa region of southern Sweden the ^{226}Ra activity level is significantly higher than that of ^{228}Ra. This may be related to the average activity ratio of ^{232}Th and ^{238}U (^{232}Th/^{238}U), which is equal to ~0.76 (Andrews et al., 1989).

Some researchers attempted modeling the processes controlling the contents of radium isotopes and their activity ratio in groundwater (Davidson and Dickson, 1986; Krishnaswami et al., 1982; Webster et al., 1995; Chau et al., 2016) and they confirm the important role of desorption/adsorption phenomena, as well as the timescales of groundwater flow. In surface and shallow water, the radium concentration is rather low and the activity ratio (^{228}Ra/^{226}Ra) higher than 1. By contrast, in deep and old water the radium concentration is high and the ratio (^{228}Ra/^{226}Ra) below 1. Because it is similar to the alkaline earth metals, the longer the retention of water in the ground the greater the mineralization and radium content. Second-hand ^{226}Ra is formed after three consecutive alpha decays, whereas ^{228}Ra is formed after only one; in consequence of the recoil effect, ^{226}Ra is more easily leached from the host rock than ^{228}Ra.

The content of radium isotopes and their activity ratio (^{228}Ra/^{226}Ra) are also determined by the water's chemical composition.

An increase of Ra concentration is often observed with increasing depth of water formation (Fig. 1.6).

Radium isotopes in drinking water have been investigated in many countries. The activity concentrations of ^{228}Ra and ^{226}Ra in

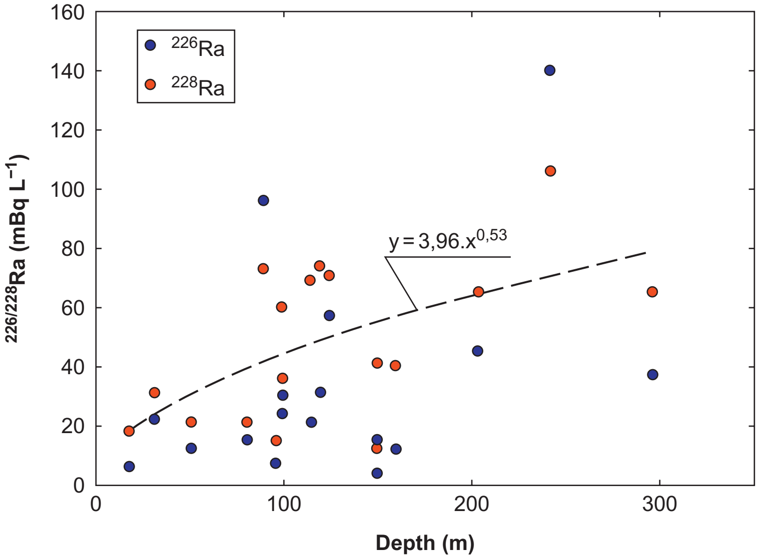

Fig. 1.6 ^{226,228}Ra concentrations in Polish Carpathian mineral waters versus deep-water formations (Chau, 2010).

drinking water from 176 drilled wells in Finland ranged from <0.03 to 0.3 Bq L^{-1} with an average of 0.034 Bq L^{-1} and from <0.01 to 1.0 Bq L^{-1} with 0.041 Bq L^{-1}, respectively (Vesterbacka et al., 2006a,b). Among a total of 1270 water samples collected from 15 principal aquifers in the United States and used for drinking water in 45 states, only 40 samples had a combined Ra ($^{228}Ra + ^{226}Ra$) concentration higher than the maximal contamination level (MCL = 0.185 Bq L^{-1}) (Szabo et al., 2012).

Due to the similarity of radium properties to other alkaline earth elements (i.e., calcium, strontium, magnesium), radium radioisotopes can easily be incorporated into bones and produce short-lived radionuclides. Many metabolic diseases such as leukemia, sarcoma, or bone cancer can be the result of exposure to radium isotopes. For the general public, the consumption of food and water containing radium may lead to the accumulation of these radionuclides in the body, contributing to a radiological dose (IAEA, 2014). Limit values in drinking water are 0.5 and 0.2 Bq L^{-1} (RMZ, 2017).

Lead ^{210}Pb

There are four natural radioactive isotopes of lead: ^{210}Pb ($T_{1/2}$ = 22.23 year) and ^{214}Pb ($T_{1/2}$ = 26.4 min) belong to the uranium series, ^{211}Pb ($T_{1/2}$ = 36.1 min) is a member of the actinium series, and ^{212}Pb ($T_{1/2}$ = 10.6 h) belongs to the thorium series. All the lead isotopes mentioned are beta-decay radionuclides. The geochemical behavior of lead isotopes is the same as stable lead and, after forming, they can react with other ions and form lead compounds in the surrounding environment. Due to the short half-life period, ^{210}Pb is of interest as regards drinking water and the environmental sciences. Generally, the surface and groundwater content of ^{210}Pb is below 1 Bq L^{-1}. Godoy and Godoy (2006) reported the measured concentration of ^{210}Pb in the mineral waters produced by 36 water plants in Brazil varied from below 10 to 510 mBq L^{-1} with an average of 19 mBq L^{-1} (Godoy et al., 2001). The same authors stated that there is a linear correlation between ^{210}Pb and ^{222}Rn in groundwaters (Godoy and Godoy, 2006). In Austrian mineral waters, ^{210}Pb ranges from below 3 up to 17 mBq L^{-1} (Wallner et al., 2008). Aleissa et al. (2004) reported ^{210}Pb in Saudi Arabian mineral waters varied from 1.3 to 7.8 mBq L^{-1}. In most mineral waters occurring in the Polish Carpathians, ^{210}Pb is below 0.5 mBq L^{-1}, but this excludes some mineral waters with high mineralization (more 10 g L^{-1}) in which ^{210}Pb reaches 350 mBq L^{-1}.The water occurs at great depth (~1000 m) and is rich in CO_2 (Chau, 2010).

The ^{210}Pb isotope is hazardous to humans not only as a heavy metal but also as a radioactive element. Under Polish legislation, the maximum content of ^{210}Pb in drinking water is 200 mBq L^{-1}.

Polonium ^{210}Po

There are seven natural polonium isotopes: ^{210}Po, ^{214}Po, and ^{218}Po that belong to the uranium decay series; ^{212}Po and ^{216}Po belonging to the thorium decay series; and ^{211}Po and ^{215}Po belonging to the actinium decay series. All polonium isotopes are alpha radionuclides. Among the natural polonium isotopes, ^{210}Po has the longest half-life of 138.4 days; the other isotopes have half-lives of only 3 min or less. Hence, the primary focus of this publication is the behavior of ^{210}Po. In the environment, ^{210}Po is present at such low concentrations that it clearly does not form separate compounds. Assuming there is secular equilibrium in the uranium series, the molar ratio of polonium to uranium (^{210}Po/^{238}U) is 8.5×10^{-11}, while the molar ratio of polonium to radium (^{210}Po/^{226}Ra) is 2.4×10^{-4}. The radioactivity of ^{210}Po in groundwater is typically <40 mBq L^{-1}, with a maximum value of 6.6 Bq L^{-1} (Seiler, 2011), which corresponds to typical groundwater concentrations of <0.001 fM and a maximum of only 0.17 fM. Polonium can occur at stable oxidation states of −2, +2, +4, and + 6, with the +4 oxidation state being the stable state in solution conditions, although Po^{2+} has also been predicted to be most stable in seawater and under reducing conditions. Polonium hydrolyses, forming $PoO(OH)^+$, $PoO(OH)_2$, and PoO_2 in slightly acidic to neutral pH regions and PoO_{2-3} in alkaline solutions. The occurrence of polonium in water can result from: (i) polonium produced from naturally occurring sources within soils in the unsaturated zone, (ii) polonium naturally deposited onto the surface from atmospheric sources, and (iii) anthropogenic sources. These sources add to the polonium carried in the groundwater by rainwater as wet deposition. The infiltrating waters then recharge the underlying groundwater systems. A certain fraction of polonium in groundwater is also generated from the host rock. Due to chemical activity, a large fraction of the activity released from mineral grains is adsorbed onto the aquifer rocks. The distribution of polonium in groundwater is therefore strictly controlled by the adsorption characteristics of the surrounding minerals. The separation coefficient of polonium between water and rock (k_d) is of the order of $n \times 10^{-5}$. ^{210}Po concentrations in groundwater are in the range 1–30 mBq L^{-1}, although values of up to 7 Bq L^{-1} have been recorded in several well waters.

Publications concerning polonium in water are scarce. Aleissa et al. (2004) report that the measured polonium contents in several aquifers in Saudi Arabia varied from 0 to 13 mBq L^{-1}, with an average value of 3.5 mBq L^{-1}. Seiler measured polonium in 63 domestic and public wells in Northern Nevada, United States. The ^{210}Po activity concentration ranged from 0.37 to 6.6 Bq L^{-1}. The concentration of ^{210}Po in Austrian mineral water varied from 0.4 to 6.1 mBq L^{-1} with 1.9 (Wallner et al., 2008).

^{210}Po can be produced by activation following the reaction ^{209}Be + $n \rightarrow$ ^{210}Bi; ^{210}Bi undergoes β decay, with $T_{1/2} = 5.013$ days, forming ^{210}Po.

Polonium is one of the most toxic elements and, under Polish legislation, the maximum permitted content of ^{210}Po in drinking water is 100 mBq L^{-1} (RMZ, 2017). Polonium can enter the human organism by different pathways such as consumption of food, beverages, and breathing in. The contribution of beverages in the human body ranges from 38% to 78%. The average biological half-life of ^{210}Po is nearly 30 days (IAEA, 2017). The highest concentrations of activity in humans are found in the lung, liver, and to a lesser extent, in the kidneys. Polonium has also been found in hair, which is a good indicator of polonium contamination in the human body. Polonium is also concentrated in bone marrow and the skin (IAEA, 2017; Scott, 2007).

Radon (^{222}Rn)

There are three natural isotopes of radon: ^{219}Rn with $T_{1/2} = 3.96$ s, ^{220}Rn—$T_{1/2} = 56.6$ s and ^{222}Rn—$T_{1/2} = 3823$ days. All the natural radon isotopes are alpha-decay radionuclides. With regard to the half-life period, only ^{222}Rn is important in water. ^{222}Rn is the daughter of ^{226}Ra and the parent of ^{218}Po. Radon is an inert gas; it shows high solubility in water and mobility in groundwater. The concentration of ^{222}Rn in groundwater varies from a fraction of a Bq L^{-1} up to several hundred kBq L^{-1} (Przylibski, 2005; Walencik-Łata et al., 2016). The concentration of radon is mostly determined by the content of radium (uranium) in aquifer formations, its porosity, and fractures; for example, in sedimentary aquifers such as sandstone and limestone the concentration of ^{222}Rn in groundwater is often below several tens of Bq L^{-1}, while in an intrusive aquifer or high-grade metamorphic rocks the Rn concentration in groundwater is high enough and reaches several hundred Bq L^{-1} or kBq L^{-1} (Erlandsson et al., 2001; Le Druillennec et al., 2010). As a consequence of ^{222}Rn decay, ^{218}Po ($T_{1/2} = 3.05$ min), ^{214}Pb ($T_{1/2} = 26.8$ min), ^{214}Bi ($T_{1/2} = 19.7$ min), and ^{214}Po ($T_{1/2} = 0.00016$ s) are formed. Both ^{218}Po and ^{214}Po are alpha-decay isotopes, which provide a major contribution to the radiological dose from the ^{222}Rn group (Porstendörfer, 1993). Radon in tap water can be released into the dwelling air by washing, bathing, cooking, and so on.

There are two pathways through which people are exposed to radon in water, from ingestion (drinking) of water, and indirectly, from the inhalation of radon and its daughter elements resulting from the decay of radon released during the use of water by a household. Exposure to indoor radon and its progeny is rather associated with a potential increased risk of lung cancer, and ingestion of radon in water is a suspected cause of stomach diseases (López et al., 2004). Mills (1990) reported that the ratio between the hazard resulting from radon ingestion and that arising from the inhalation of radon and its progeny is 1:5 and the release coefficient of Rn from water into air is 1×10^{-4} (Mills, 1990). In European Union countries, the maximum Rn level in drinking water is $100\,\mathrm{Bq\,L^{-1}}$ (RMZ, 2017).

1.3 Treatment of Natural Water

It is well known that the content of chemical, radioactive elements as well as organic compounds in natural water varies over a very broad range. In order to eliminate harmful organic compounds and keep mineralization and its chemical composition within the legislative range, natural water needs to be treated. Nowadays, a number of technologies are in routine use for this purpose. The treatment technologies consist of filtration, aeration, coagulation, co-precipitation, ion exchange, and even reverse osmosis. In most countries in the world, tap water and bottled water are treated (Almássy and Buzás, 1999).

1.4 Conclusion

The worldwide market for the use of mineral and bottled water is growing year on year. As a trend toward a healthy lifestyle becomes increasingly popular, many mineral water brands are marketed in developed countries. Statistical analysis showed that by the 2017, people all over the world are expected to consume about 391 billion liters of bottled water.

In many cases, this water is extracted from clean, natural geological sources. Mineral water contains a combination of the main cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), anions (HCO_3^{-}, Cl^{-}, SO_4^{2-}), and specific compounds (which can determine the medicinal value of water) in varying amounts. These dissolved components can bring varied health benefits to conditions like cardiovascular diseases and nervous exhaustion (bicarbonate water). As a consequence, some mineral waters in their natural state may be considered as “dietary foods for special medical purposes”. This includes natural waters or their concentrates containing ingredients such as iodides, fluorides, calcium, magnesium, and sodium in significant concentrations from the point of view of the physiological functions of the human body.

However, apart from high-quality natural water, some of them may be exposed to contamination. The presence of heavy and radioactive elements in water is controlled by natural processes and human activity. The natural processes include ore, coal, crude oil, and natural gas deposits, rock formations, and in some parts of the world also the toxic products of volcanic eruptions and hydrothermal activity, the interaction between rock and water, and the physical and chemical properties of flowing water. Human activities include mining mineral deposits, old mines, mine waste piles, tailings, mineral processing wastes, mine and process wastewater ponds, fertilizers used in agriculture, smelting factories, and lagoons which have a detrimental impact on all water reservoirs, especially the surface water reservoirs. Another problem related to coal burning is the release of methane, carbon dioxide, hydrogen sulfide, and sulfur dioxide from abandoned workings into the atmosphere, which then releases toxic compounds attached to the water particles forming rainwater and migrating to surface and groundwater. Hazardous and toxic materials are apparently related to drinking water contaminated with heavy metals such as Pb, Cd, Cu, Mo, Ni, and Cr and radionuclides. High-level contamination of the above-mentioned elements leads to renal failure with liver cirrhosis, hair loss, chronic anemia, sarcoma, bone cancer, and so on. Heavy metals and radionuclides should be removed from drinking water if they are present at high levels to improve human safety.

To solve the above-mentioned problems, toxicology studies should be incorporated into national strategies worldwide. They should cover the detailed locations of potentially toxic areas by identifying the locations of industrial plants, and their solid, liquid, and gas wastes, and combining this information with geological, geochemical, and biogeochemical, and geophysical surveys, as well as biological reclamation of mine waste piles, biological remediation, fertilized areas, adjustment of land-use management plans to the environment, etc. These practical ventures should be backed up by basic studies on the natural behavior of toxic substances in the hydrosphere, and the rock-soil-vegetation-atmosphere system, including water-soil and water-plant interactions, within similar rock and soil profiles in differently polluted areas. These studies should be carried out in parallel with the assessment of heavy metal and radionuclide concentrations in natural drinking waters, and of their impact on animal and human health.

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2

THE WORLD AROUND BOTTLED WATER

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2.1 Introduction

Water is the main constituent covering 71.4% of the earth. But irresponsible and nonsensical use of water makes it unavailable for future generation (Kulshreshtha, 1998). Pure water is soft with no characteristic smell; but when it comes in contact with soils on the surface of the earth, different chemical reactions occur and different useful minerals dissolve to render it hard. We cannot live without water, it helps to maintain body temperature by sweating and is the main part of blood to provide nutrients to different parts of the body. Water is used in many different ways which include: washing, gardening, cleaning, etc., but use of water for drinking purpose is the most important one. Water makes up about 60% of body weight in men and 55% in women and for infants it is about 70%–80% (Miller, 2006). Water is, in fact, incredibly important aspects of lives.

Drinking water quality is mainly determined by standard total dissolved solid (TDS). Different country has different regulation for the TDS level, in United States it is 500 mg/L while in India it is 250 mg/L. The TDS actually comprises inorganic salts and small amount of organic matters dissolved in water. Main constituents for TDS are cations of calcium, magnesium, sodium, and potassium and anions of carbonate, bicarbonate, chloride, sulfate, and nitrate (Daraei et al., 2015; Abouleish, 2012). Some organic matters also profoundly contribute to the TDS of water. World Health Organization (WHO) has set different TDS level for drinking water (Table 2.1). With the passage of time, the concern over of quality of drinking water has grown rapidly and bottled water has gained increased popularity. Bottled water has now become the synonym of drinking water, packaged in bottle. Bottled water of all brands is colorless, but it differs in taste because of different water source. Manufacturers in the rudimentary stage considered bottled soda as the option in lieu of water, which, however,

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Table 2.1 WHO Guidelines for TDS Values to Determine Quality of Drinking Water

S. No.	TDS (mg/L)	Quality
1	Less than 300	Excellent
2	300–600	Good
3	600–900	Fair
4	900–1200	Poor
5	Above 1200	Unacceptable

suffered from few drawbacks. People realized that regular use of soda may be detrimental to health and the need for bottled water was seriously felt. Consequently, there has been commercialization of water in bottles and attempts to introduce bottled water as a healthy drink.

United Kingdom was the pioneer in bottling water. In 1621 Holy Well bottling plant started bottling mineral spring water. The commercial distribution started in Boston (USA) in 1767 in Jackson's Spa. The popularity quickly led to a market for imitation of products. In 1809, Joseph Hawkins was issued the first US patent for imitation mineral water. In the beginning, people considered bottled water to possess some therapeutic properties that could help to treat many common ailments. In the 19th century large usage of bottled water was recorded when municipal water supply was contaminated with pathogens like cholera and typhoid. Today bottled water is the second most popular commercial beverage in the United States. Carbonated water is, however, still in the market along with flavored bottled water. It has been customary in recent days in most of the countries worldwide to use bottled water; but in most cases it is not driven by health concern. It is not guaranteed that bottled water is safer and cleaner than tap water. The consumption of bottled water has by and large been reliant not on the brand loyalty rather on differences in believes, perceptions, and according to its use (Wells, 2005; Gorelick et al., 2011). Consumer's choice to purchase bottled water has mainly been dependent on quality, health, environmental concern, convenience, price considerations, and most importantly lifestyle. Bottled water includes well, distilled, mineral, and spring water. It may be carbonated or noncarbonated. Bottled water is often stored for emergencies like natural disaster. Mobile treatment units have also been developed for the distribution of drinking water in small polythene bags, but for prolonged storage it has been proved to be not good for health. Engineering and technologies of bottled and packaged water are quite related to its manufacturing, distribution, and supply of quality water purification system. These are important for designing and manufacturing the finest and most economical water. Bottled water industries do not require high manufacturing process and is based entirely on energy requirements for pumping, filling, treatment, and storage, etc. (Gleick and Cooley, 2009). The required energy for the water treatment plant can also be fulfilled by solar and wind energy (Chen et al., 2008). In 2015, manufacturing by Nestle Waters generated 22 g CO_2 eq/L and required 0.22 M of energy per liter. India is the 10th largest bottled water consuming nation in the world. The 20-L bulk water jars have found phenomenal acceptance in household and work place. Bottled water is "not guilty" in terms of environmental issue or social blight. Bottled water does not deserve to be banished from Quaker circles as a sign of spiritual, moral, and ecological depravity: The users are not heedlessly ruining the planet. It is much safer than normal tap water although the use of plastic bottles make it somewhat unsafe. Glass containers are primary alternatives of the plastic bottled in recycling terms. But glass bottles are not user-friendly especially for kids since they cannot carry these safely and broken glasses can cause more injuries compared to plastic bottles. It is, however, not directly or indirectly related to world's water problem. Even if bottled water vanish in the near future, the water consumption rate of the world would not have any significant impact.

Bottled water is very important, in the case of natural disasters or any other emergency preparedness. It is fully portable and versatile such as its use makes our life more convenient in today's rushed lifestyles. Bottled water is ideal consumer product since it is nonaddictive, alcohol-free, caffeine-free, colorless, odorless, and flavorless. The present review addresses all necessary aspects of bottled water.

2.2 Types of Bottled Water

According to origin bottled water can be classified as:

1. *Artesian well water*: Water may be obtained from underground water source under high pressure. Artesian aquifer is a layer of sand, gravel, rocks, and clay and water rises out through these layers of the outer surface by hydrostatic pressure.
2. *Mineral water*: Natural mineral water is obtained directly from the underground sources and it is collected directly from there and packaged without further treatment. Therefore, sometimes water of this kind is also called "pure water" or "untouched water."
3. *Spring water*: Spring water is obtained through a particular source, either underground or surface. Water source is protected to prevent water from pollution and it is also used without treatment.
4. *Well water*: It is the most common natural resource of water and it is used after treatment.

5. *Tap water*: Tap water is obtained from concerning river of the particular region and it can be directly bottled after treatment, like chlorination.

2.3 Bottled Water Versus Tap Water

It seems paradoxical that people decide to package and sell and buy something that is freely available; they prefer more expensive and less comfortable water source for drinking purpose. While there is no universal standard for drinking water, WHO gives guidelines for drinking water (WHO, 2017). The standard varies from country to country. Bottled water is consumed for many different reasons including taste, convenience, poor quality of tap water, and safety issues including health concern and search for a substitute for sugary drink (Chiarenzelli and Pominville, 2008). Main reasons behind increasing use of bottled water instead of tap water are as follows:

1. *Organoleptics*: The factors which affect the taste of water create dissatisfaction in people. People, in general, prefer sweet water.
2. *Health and risk*: Apart from taste, health-related issues are mainly accountable for water consumption (Abouleish, 2012); there is a common belief that bottled water is healthier than tap water. Tap water has mainly three types of contaminations: chemical (pesticide, drug etc.), physical (due to mud, sad, color, odor), and microbiological (bacteria, viruses etc.). People prefer bottled water to avoid eventual tap water risk (Napier and Kodner, 2009; Anadu and Harding, 2000).
3. *Brand name*: Most of the people nowadays are crazy for brands and style. While outside they prefer drinking bottled water rather than tap water for social status, not because of much concern about safety and health issues (Wilk, 2006).
4. *Logistic based*: Sometimes, during long journey, good quality of water is not readily available en route and bottled water becomes very important (Akabogu, 2014). Consumer’s preference may vary depending on location, such as tap water is preferred at home, while bottled water at work. It also depends on the intended use such as to make tea, to prepare food, or to drink directly. Use of bottled water or tap water is also sometimes based on human psychology (Gregory and Di Leo, 2003).

Bottled water industries lowers harm as well as decreases the fear level. In practice, beverage companies play with consumers’ fears of illness and contamination from tap sources. One major player in the assault on tap water is Brita filters, with the commercial ads that use “Tap and toilet water come from the same source. Don’t you deserve better?” The perceptions of healthiness, as stated earlier, are influenced by organoleptic (taste) (Grondin et al., 1996). Not surprisingly, consumption of bottled water is sometimes higher in communities that have serious problem with tap water; sometimes, tap water has excess metal ions such as Cd, Hg, As, etc. (Jakus et al., 2009; Bakurdere et al., 2013). Advanced knowledge on the factors that contribute to the use of drinking water can contribute to a better understanding of the consumers concern and behavior (Roche et al., 2012). Bottled water is, in fact, far from being an alternative to tap water. It seems to be mostly consumed as a substitute for alcoholic and traditional soft drinks. The environmental impact, container safety, water origin, emergency supplies, and role of the bottled water industry continued to be area of concern for many people. A qualitative study has been performed using semi-structured interviews, with 23 users from the Munrow sport center in the Birmingham campus. The study reported that most of the people chose bottled water for health benefits but they don't know about its nature (Ward et al., 2009). Sometimes because of marketing campaigns, people choose bottled water instead of less healthy beverage. Bottled water provides a safe, convenient, refreshing, and responsible choice.

Risk factors associated with tap water include perceptions that it is not safe for drinking, the fear that water will become contaminated through leaked pipelines and can cause illness to anyone. It is always considered better to treat tap water before use like boiling, simple filtration, etc. and most of the studies showed that bottled water is not healthier than tap water (Rowell et al., 2015; Howard, 2003). Most convincing evidence comes from a study by National Resources Defense Council (1999), and the report concluded that "There is no assurance that just because water comes out of a bottle, it is any cleaner or safer than water from the tap." In Iran a comparative study was performed between tap water, bottled drinking water, and point of use to find suitable water for drinking purpose (Dindaroo et al., 2016). In fact more than 30% bottled water comes from the tap, sometimes further treated and sometimes not. Bottled water is therefore not necessarily better or worse than tap water; it only depends on specificity of the particular cases.

2.4 Bottled Water Industry

Unfortunately sufficient safe potable water is not available everywhere. Either harmful chemical is found in the soil layer or it may be contaminated by pathogens, bacteria. If such water, enter in to the body, we get infected and suffer by waterborne disease. It has thus been imperative to process and bottle safe potable water for human consumption in prevailing conditions. Thus, shortage of pure water around the world has opened new avenues for bottled water. Bottled water industry does not require high-cost processes; it involves a relatively light manufacturing process. Bottled water industry, through their long campaigns, has created awareness and people want bacteria free and odorless water as a health drink. Of course, bottled water is healthy and there is no direct impact on the environment by water present in bottle. However, use of plastic bottles creates environmental risk. They comply with local and state regulatory framework, which applies to other water users in the same class and will continue to do so.

Bottled industry provides mainly two types of packaged water.

1. *Packaged natural mineral drinking water*—Packaged natural mineral water showed presence of less than 250 ppm of TDS (Whelton et al., 2007) (IS 14543, Indian standard code). Natural mineral water can further be divided into two subclass, that is, premium natural mineral drinking water and natural mineral water. Examples are San Pellegrino, Evian, Perrier, Himalayan, Catch, etc.
2. *Packaged drinking water*—Packaged drinking water is water derived from any source of potable water (well, bore well, ground water, etc.) which may be subjected to different treatment processes such as decantation, filtration, aeration, reverse osmosis, etc. By all this processes water will get disinfected for a long time period (IS 13428, Indian standard code). Examples are Parle, Bisleri, Coca-Cola, Kinley, Aquafina, etc.

Bottled water industry process disinfect water by means of chemical or physical processes, for example, ozonation, ultraviolet treatment, silver ionization, etc. The development of microorganism is controlled to a level that is suitable for consumption. The processed water is then filled in sealed container of various size and shape for further direct consumption. Packaging material should be thermo-proof, tight, and impervious.

In India, the bottled water industry boomed in the late 1990s, just after Bisleri launched its packaged drinking water. After that several companies have come up, that is, Aquafina, Tata water plus, Kinley, Himalayan, Bailley, Kingfisher, etc. Due to perceptions made by bottled water company overall sales growth and consumption has increased tremendously. Parle Bisleri is the market leader in India. It shares more than 45% in the branded bottled water, while Coca-Cola Kinley comes second with 15% share (Dhal and Mitra, 2015). Bottled water industries have also grown in other countries, for instance, Lebanon has one of the highest growing consumers of bottled water, and New Zealand allowed fluoride in bottled water. Bottled water industries, for the competitiveness in the market, need to lower the price (Woods, 2009) even by sacrificing or adjusting some of desirable quality parameters through some sort of flexibility. Some industries focus on people's taste and therefore they reduce TDS of water since a low TDS value gives sweetness to water. Among all the brands of bottled water Nestle and Coca-Cola are the leading bottled water manufacturers in world.

The global bottled market was valued at more than US$170.0 billion in 2014 and is expected to reach US$280.0 billion by 2020 (Deerfield Beach, 2017). The bottled water market is a witness to rapid growth of civilization and indicates high awareness for cleanliness. Fast growth of tourism and portability of hygienic bottled water trigger demand for bottled water. However, stringent regulations regarding packaging of water and bottled water standard are expected to hamper the growth of the market to some extent.

2.5 Manufacture of Bottled Water

Water is a very sensitive product on both microbiological and chemical levels. One of the main challenges faced by bottled water processing is to consistently produce a quality product free of pathogenic organisms and protozoa that may change its quality, reduce its shelf life, and become a pathogenic threat to customers. Sometimes bottled water obtained from surface water sources or plant may have a more consistent taste than tap water. Strict production control is critical to avoid any contamination of pathogenic bacteria or protozoa. Water treatment plant processes water according to quality of raw water and requirement of the region. Plants treat water following different processes. Common processes are: coagulation, filtration, and disinfection. Bottled water processing, in general, consists of the following steps.

1. *Filtration*: Water must be free of any contaminants that may spoil its quality.
2. *Tank venting*: The air in the storage tank must be free of microorganisms to ensure that the stored water is not contaminated.
3. *Carbonation*: Carbonation is the step of adding carbon dioxide to water. It is used to produce sparkling water. The CO_2 that is injected into water must be free of particles and microorganisms.
4. *Bottle blower and bottle washer*: To maintain the quality of the water and its shelf life, use of a safe and reliable container is essential. The air used in the bottle blower to turn the preforms into the final PET bottle must be free of contaminants; its filtration ensures a bottle with low bioburden is produced. Bottle blowing can be done during any stage of the process using PET bottles. The water used to rinse PET bottles must be free of contaminants; its filtration ensures good quality of the bottles prior to filling.
5. *Bottle filler*: Gas filtration can also be used during the filling process of carbonated drinks. In order for the filling to be possible, the filler bowl must be pressurized, and it is essential that the gas used is microbiologically stable.

   Bottled water manufacturers have reduced the thickness and material quality of bottle; they also have focused on comfortable structural design (Fig. 2.1).

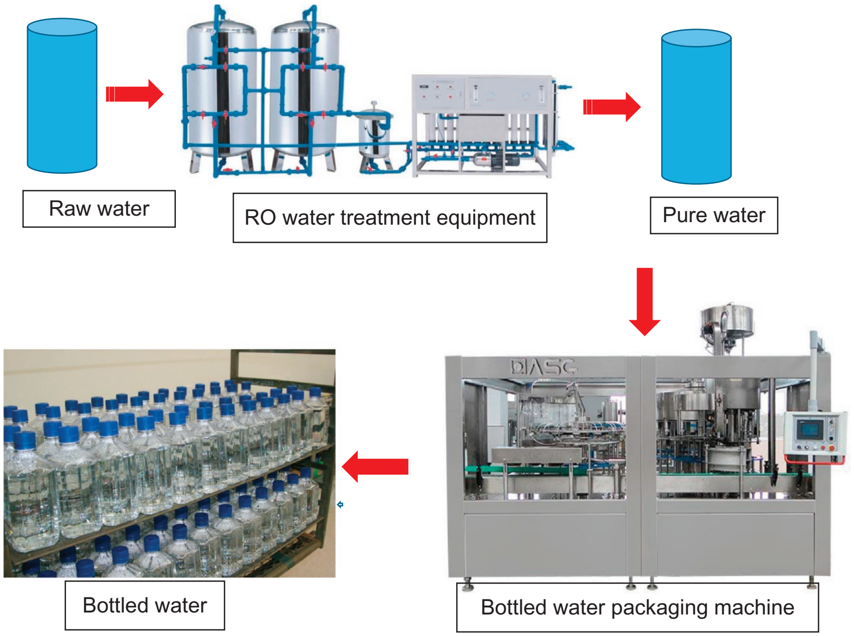

Fig. 2.1 Manufacturing of bottled water.

The PET is modified by copolymerization by the use of added co-monomer. The PET is relatively strong, withstands high temperature, and has good barrier properties against moisture, oxygen, CO_2, alcohol, and solvents. It can be made transparent by limiting crystallinity using copolymerization, by adding fillers, or by controlling cooling when melt processed during manufacture. The PET bottles made for filling water are amorphous with low crystallinity for clarity and toughness. It has highest recycling rate.

2.6 Labeling on Bottled Water

In most of the cases, it has been shown that bottle water is actually tap water. However, it is also a matter of contention that the quality specifications for some bottled water in some jewels jurisdiction are more stringent than the standard for tap water. Sometimes bottled water is mentioned as distilled water or purified water. There are different terminologies written on the bottled water for packaging material (Table 2.2). Label on bottled water should clearly mention following information: brand name, type of bottled water, source of water, ionic composition, volume, bottling, expiry date, company name, address, country name as well as treatment strategies employed. For convincing people, bottled industries offer a variety packaging options: 100,

Table 2.2 Description of Plastic Containers Used for Water Packaging

S. No.	Types of Container	Description
1.	Jar	Reusable plastic container
2.	Bottle	One time use plastic container, to be crushed after use
3.	Cup	Cup/glass shape tumbler, one time use plastic container, to be crushed after use
4.	Glass bottle	Container made of glass, can use after sterilization

500, 750 mL, 1, 2, 10 L, etc., in plastic bottles which is made up of PET, the first plastic bottle able to withstand the pressure of carbonated liquids (patented by Hawkins, 2011). Bottled water contains mainly four different ingredients: magnesium sulfate, potassium chloride, and salt alongside purified water on nutrition facts label. Smart water contains calcium chloride, magnesium chloride, and potassium bicarbonate.

2.7 Energy Requirement for the Production of Bottled Water

Energy is required by bottled water throughout its life cycle: from water collection through treatment to package, temperature control, use, and recycle of plastic bottle. It is difficult to calculate a standard total amount of energy required, because it depends on many factors, including location, type of material, distance between manufacturer and consumer (Chesson et al., 2010), water sources etc.; among these only two factors, ways of transport and plastic bottle manufacturing process, mainly contribute to energy requirements (Anable et al., 2006). The PET is embedded with energy, but its conversion into bottles requires additional energy, which comes from natural gas, petroleum, and electricity, 70–83 MJ (thermal) kg^{-1} of PET resin (Gleick and Cooley, 2009) barrel oil having 6000 MJ kg^{-1} (Burton, 1996). Production followed by performance and rendering them into bottles require an additional energy 20 MJ kg^{-1} of finished bottle, thus total energy consumed is approximately 100 MJ kg^{-1}. Total weight of a PET bottle with cap is ca. 40 g. If 40 g PET is required to make 1 L bottle then 4 million tons of PET will be required to produce 100 billion liters of bottled water containers. Most of the manufactures, for example, Nestle, Coca-Cola, etc., have been trying to reduce weight of PET bottles (Tandon et al., 2014).

In summary, energy is required mainly for the production but if distance is more than production, energy become less; while far less energy is needed for the processing, cooling, and treating water.

2.8 Consumption of Bottled Water

Bottled water has been rapidly transformed from niche market into ubiquitous consumer object (Jafee and Newman, 2012); the explosive growth of bottled water is expected to continue. Bottled water has been widely consumed due to convenience and cleanliness (Cidu et al., 2011). The industries are trying to make more thin and lightweight water bottles with clever structural design to increase its consumption. Bottled water of various sizes and volumes predominately made of plastic are produced for public consumptions. In particular since 1990s, bottled water has become a major global commodity available in every corner of the world. From technology perspectives bottled water can be considered a decentralized technology which can distribute water for human consumptions via a portable container, that is, bottle, instead of a pipeline which is required component for transporting water in conventional centralized water infrastructure.

Consumptions of bottled water have sky rocketed in recent years. The global consumption of bottled water reached 230 billion liter in 2010, and has grown faster than 6% per year. In 2016, Mexico recorded a maximum consumption of 67.2 gal or 354 million liter bottled water and the consumption is expected to reach 356 million liters in 2018. By the end of 2017, people are expected to have consumed 391 billion liters. According to “Zion market research” global bottled market value was USD 170 billion and is expected to rise. Thus bottled water consumption has been growing at global level (Muhamad et al., 2011). Earlier bottled drinking water was privileged to high class people, tourists, and highly health conscious people. Therefore, initially bottled market had been crawling at the rate of 3%–4%; but within few years its popularity increased significantly with life style (Sharma and Bhaduri, 2014). People, at present, spend more money on their life style. This tremendously increased the consumption of bottled water. This was reflected in the consumption of bottled water in United States from 1998 to 2016 (Fig. 2.2). In 2007, it was 212 billion liter, which rose to 288 billion liter in 2012, and it was expected to reach 391 billion liter in 2017. Among all countries, Mexico had highest bottled water consumption during the same period (64.5 gal). Asia Pacific had 30% consumption among total consumption of bottled water in the world. The reason behind this consumption is economic growth and life style of people. While, North America and Europe are expected not to grow too much even declination may not be surprising

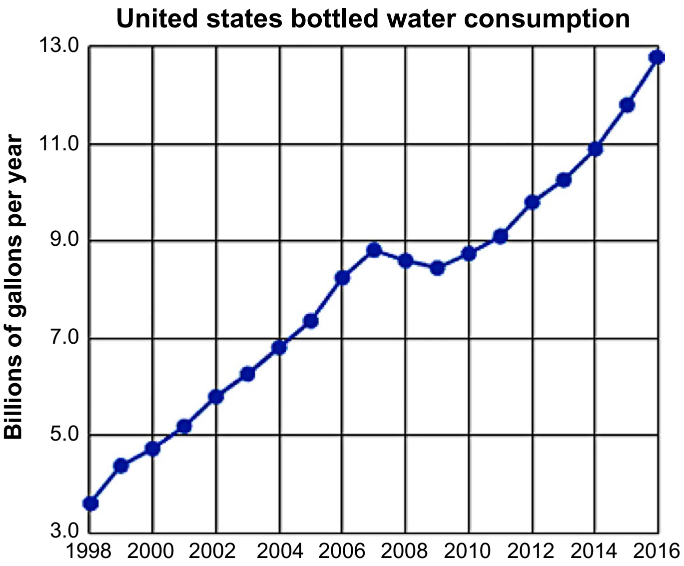

Fig. 2.2 Consumption rate of bottled water in USA. Image taken from geology.com.

for bottled water consumption. Latin America and the Middle East are also expected to witness the robust growth of bottled water market in the years to come. Overall, the reason for bottled water consumption seems to vary. The consumers are now comfortable and ready to use bottled water irrespective of whether it is branded or nonbranded. Some important factors considered are brand, packaged size, shape, convenience, durability, cost, competitive based, and life style, etc. Variety is spice of life, therefore, bottled industries attract people by several ideas. Some companies prefer branding advertisement while others focus on health-based advertisement. The three major reasons behind consumption of bottled water are cost leadership (low), differentiation, and a focus strategy. We can get 300 mL water without glass for Rs. 1. while with glass it will be Rs. 2. Water vendor provides water where water is scarce or there is lack of available drinking water. Water vending refers to many forms of selling water, like water kiosk, tanker, trucks, etc.

2.9 How to Reduce Bottled Water Consumption

Excessive use of bottled water increases environmental problem such as water wastage, pollution, and climate change (Bates et al., 2008; Gornall, 2017). Use of bottled water could be reduced by public awareness campaign (Samadi et al., 2009) or by showing them movie "how to save water." The drawback of excessive use of bottled water may be explained and necessity and usefulness of tap water for our health may be made understandable (Saylor et al., 2011). There should be campaigns for traditional information based on the grounds that enhance knowledge and understanding of environmental issues that lead to change in behavior.

2.10 Water Quality Indices

Water quality indices are useful tools for the determination of overall quality of water (Tsakiris, 2016; Abbasi and Abbasi, 2012). It is taken by decision makers and stakeholder for water quality issues (Toma et al., 2013). These indices are necessary for the improvement in water quality in which a single figure represents all characteristics of water. The first water quality index was proposed in 1965, in which 10 parameters were included. The most important and widely used water index was developed in 1970. In India, the Bureau of Indian Standards formulated Indian Standard for packaged drinking water and packaged natural mineral water. Water quality has a major impact on human health, (Cemek et al., 2007; Chiarenzelli and Pominville, 2008). Selection of parameters for the water quality indices is a very critical task. Bottled water quality index includes two stages: first one is to test pH and absence of bacteria, *Escherichia coli* and second stage involves determination of five subindices: nitrates (NO^{3-}), nitrites (NO^{2-}), chloride (Cl^-), sulfate (SO_4^{2-}), and electrical conductivity at 20ºC (Table 2.3). Quality of bottled water is controlled by Food and Drug Administration while tap water is controlled by Environmental Protection Agency.

2.11 Environmental Risk

Bottled water is sold in containers ranging from 500 mL to 50 L. Small bottles are popular in school, office, and in small gathering while big containers are used daily in home, offices, etc. Most of the bottled water containers are made up of recyclable PET plastic. It is a thermoplastic resin, which is 100% recyclable; but rarely, if not always, a small fraction of it is recycled (Boateng and Frimpong, 2013). Definition and environmental cost of transportation of bottled water has been another concern. As the size of the container increases consequent release of carbon dioxide and other hazard may affect climate. Since we are living in the age of "thirsty world," we should take care of water. Furthermore, many people are unaware of the negative effect of PET bottle on human as well as aquatic health (Simon, 2010).

Table 2.3 List of Bottled Water Quality Indices and Their Maximum Allowable Limit

S. No.	Parameters	Unit	Maximum Allowable Limit
1.	*E. coli*	Number/250 mL	0
2.	pH	pH scale	6.5–9.5
3.	Nitrates (NO_3^-)	mg/L	50
4.	Nitrites (NO_2^-)	mg/L	5
5.	Chloride	mg/L	250
6.	Sulfates	mg/L	250
7.	Electrical conductivity (20°C)	µS/cm	2500

It directly affects the climate (Samadi et al., 2009; Yang et al., 2011). We should focus our research on the bottled water consumption (Trumbo and O'Keefe, 2005). For the production of 1 L of bottled water, we need 1.32 L of water; additional 0.32 is used for processing. Therefore, we are consuming extra water, which turns into waste water. Used bottles, which we throw randomly anywhere, may take 1000 years to degrade and even in some cases they release toxic fumes and become litter. Most of the cities in the United States and Canada have banned the use of bottled water due to environmental risk from the bottles. Only one out of five bottles are recycled. Manufacturing of bottled water and destruction of used bottles by incineration pollute air, land, and water, and finally toxic fumes affect the health of the workers. Some bottled water industries uses other than PET bottles, which are nonbiodegradable and get accumulated in land and water. Worldwide fund for nature bracket (WWF) and Greenpeace have warned of the huge environmental footprint of the plastic in which water is packaged. Use of bottled water not only questions our intelligence and affects wallet, but also affects the environment. Our human fish tank gets cloudy since we throw used bottled recklessly. Also PET is nonbiodegradable; it is photodegradable and decomposes into small fragments which absorb toxins and pollute our waterways and soil. These are harmful to human and animals; sometimes toxic antimony, found in PET plastic bottles, can leach from water bottles and cause dizziness, and depression and higher amount can cause nausea, vomit, etc. Plastic bottles and plastic bags are major contributors to pollution rise in beach side. Every square mile of the ocean has more than 50,000 floating pieces of plastics, which disturbs life of ocean creatures. Sometimes they migrate. Only 23% of PET is recycled every year, rest is dumped either on land or into water stream. Therefore, majority of evidences show that use of bottled water is worse for us, definitely it gives us better option for healthy water but in the other way it causes more and more harm to environment. Sometimes we leave water bottles in car and plastic leaches into water it holds. Thus, production and consumption of bottled water has proven to be wasteful and unsustainable.

Fluoride detection level in bottled water is lower than that of tap water, and only 27% of the tap water samples were reported to contain fluoride at recommended level for optimal dental health (Varela et al., 2015; Butani et al., 2008; Johnson and DeBiase, 2003).

Bottled water companies are wasting resources and exacerbating climate change. Transport is the fastest growing source of greenhouse gas emission and transporting water adds to that.

The number of domestic and foreign tourists is increasing every year, which will increase bottled water sale in the whole world.

Finally, as the temperature increases the compression strength of water bottles decreases. Nowadays, bottled water industry is trying to make thinner and lightweight bottles, thus effects of temperature become more pronounced. Bulging at the bottom affects the functionality of bottles. Thus design also has great impact because its shape affects the bulging.

2.12 Suggestions for the Future

Bottled water does not have any side effect or cause any harm to human body. But the use of bottles affects our environment and energy and also raise the cost by factors such as plastic bottles manufacturing, water packaging, transporting, etc. (Gleick, 2011). It is better to use bottled water only on emergencies like natural disaster or during travel. Use of bottled water is recommended only when pure drinking water is not easily available and water from other available sources may cause harm to us.

Individual local actions such as avoiding bottled water are needed to help curb mounting pollution. If you are satisfied with tap water just boil it before use at home. So, stop buying bottled water and drink freely and easily available healthy tap water. Getting rid of bottled water may help keep our Earth and wallet green.

2.13 Cons and Pros

“Every coin has two sides” positive and negative, similarly, there are some cons and pros of using bottled water. Here we deliberate some cons and pros of using bottled water:

It is the best option to get drinking water, when we are outside. It is more portable, durable, and flexible to use. It is very convenient to carry and therefore very useful especially where the quality of drinkable water is not good. In addition, it is readily available and we can purchase it from anywhere and at anytime according to our need. Most important fact about bottled water is that it does not expire or have a long expiry date, so it can be ideal during disaster or for emergency situations. It has better taste than normal tap water because of treatment processes. Production of bottled water is strictly regulated by food corporation for it to be clean and free of contaminants. It is easily available at grocery stores in various sizes and price, according to the consumer's need.

But process of purifying, bottling, advertising, transporting, and storage increase the actual cost of water. Therefore, it is significantly more expensive than tap water. Generally, plastic bottles contain Bis phenol A, sometimes due to high temperature of the environment this is leached into water, which affects human body. We know that water bottles are mainly made of PET, which is 100% recyclable but most of its part is dumped on the land or into the river/ocean etc. Thus, it creates pollution on land and in water. Fluoride is significantly more likely to be detected in tap water than bottled water, this is the reason for higher prevalence of dental caries in children nowadays. Bottled water costs around 1000 times more per liter than high-quality municipal water. Production of bottled water increases the use of fossil fuels. Manufacturing of plastic bottles consumes more water than it takes to fill your own water bottles.

2.14 To Know

A. In 2009, the small New South Wales town of Bundanoon became the first town in the world to ban the selling of bottled water.
B. In 2012, the town of concord Massachusetts became the first town in the United States to ban the sale of bottled water.
C. Joseph Priestley made his first contribution by dissolving carbon di oxide in water. He discovered oxygen in 1775. Then he developed aerated waters on a commercial scale.
D. First natural mineral water was sold in pharmacies in the 17th century as medicinal water.
E. In 2016, Sikkim (India) announced ban on the use of plastic bottles.
F. Energy waste during bottled water production to consumption would be enough to power 190,000 homes.
G. As per doctor's suggestion, we should drink eight glasses of water per day, in the United States tap water cost equals $0.49 per year but the same amount of bottled water would cost $1400.

2.15 Conclusion

In summary, tap water is healthier, more environmentally sustainable, and equally logically sound than bottled water. Yet many people remain generally unaware of the negative health and environmental impact associated with water, and so, we have to investigate the means to reduce consumption of bottled water. People are comfortably ready to pay for freely available water in form of packaged water without having complete knowledge of it. Advertisements and branding enhance public to use bottled water. Mainly branded bottles are preferred than any other packaged water. Huge amounts of energy are needed for the production to consumptions of bottled water. Treated tap water or natural mineral waters are packaged in PET made plastic bottles, sometimes due to temperature variation, low and high, it may get leached into water, which is toxic to humans. Used bottles never get 100% recycled and therefore, mountains of plastics in most of the tourist places are dumped, which directly or indirectly affect the human as well as aquatic life. Of course water inside the bottle is not as harmful as the container, bottle. Finally, we should minimize the consumption of bottled water to protect our environment, ourselves, animals, aquatic life, etc.

Thus, overall it is concluded that beliefs about health, taste, water quality, life style, the environment all highly boost the consumption of bottled water. Moreover, easy availability of tap water and increasing concern regarding plastic bottles have now become a challenge for industry.

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Conflict of Interest

All authors declare that we have no conflict of interest.

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STUDY OF WATER QUALITY OF PACKAGED AND MUNICIPAL SUPPLY DRINKING WATER WITH PERFORMANCE EVALUATION OF STAND-ALONE FILTERS

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3.1 Introduction

Water is a natural resource which is extremely essential for the survival of all living organisms. Life without water is not possible on this planet. That is why drinking water needs to be safe from any type of contamination with respect to bacteriological and physiochemical parameters. Drinking water should comply with the requirements of chemical substances and physical characteristics as per the Indian standard. World Health Organization (WHO) emphasizes safe and sustainable supply drinking water for the protection of public health as per its guidelines (WHO, 2011).

Sources of drinking water in Indian cities are surface water (river, pond, etc.) and ground water (tube well, dug well, etc.). Generally, municipal authorities supply drinking water after treating surface water. On the other hand, the ground water obtained through tube well and dug well are not treated at individual or community level.

With rapid urbanization and increase in population the water demand for drinking and domestic uses are increasing day by day. In urban areas communities face acute shortage of drinking water. Municipal authorities, though take care of maintaining proper

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quality of drinking water before supply conforming to relevant Indian IS code by means of necessary treatment, sometimes they may have some risk of being contaminated and polluted due to leakage in pile networks and other causes. Ground water is generally considered to be much cleaner than surface water but manmade activities are responsible for its pollution. Pollution refers to the contamination of water by foreign matter such as microorganisms, chemicals, and industrial or other waste or sewage. Such matters deteriorate the quality of water and render it unfit for intended use. The water quality is the most important parameter of any water supply planning and also is a function of physical, chemical, and biological parameters. According to WHO (2011), about 80% of all diseases in human being are caused by water.

To minimize the pollution of drinking water and with a view to have zero risk many agencies and entrepreneurs have developed different types of water purifiers in order to get pure drinking water for domestic residences, educational institutions, offices, etc. These purifiers are developed based on various technologies such as reverse osmosis (RO), UV with normal stand-alone filter system, and only normal stand-alone candle filter. The RO and normal stand-alone filters are mostly fixed on wall having an input water provision. These two purifiers are very popular nowadays in urban areas and thus vendors rush to sell it. Besides, stand-alone candle filters, normally fixed with cylindrical container are very common since last many years for domestic residences in urban areas among the low- and middle-income groups. In this study, the performance and efficiencies of these purifiers of various brands are verified to get an actual picture. For performance analysis, quality parameters of drinking water both before and after filtration through them are determined.

On the other hand, many entrepreneurs are carrying on business of packaged drinking water (PDW) by means of production and vending in order to augment the situation of shortage of drinking water at urban areas. It became most popular among consumers nowadays owing to good marketing strategy, easy availability everywhere around any urban area, and comparatively better quality than any other sources (surface/groundwater). PDW (other than packaged natural mineral water) are water for human consumption and may contain minerals, naturally occurring or intentionally added, carbon dioxide, naturally occurring or intentionally added, but shall not contain sugar, sweetness, flavors, or other food stuffs (IS 45543, 2004). Also many researchers carried out studies to assess the quality of PDW and it was stated that bubble top can PDW was found to be contaminated compared to bottled water (Sudarsan and Renganathan, 2012). It was also observed that sachet-packed water sold in Nigeria and India had not met the microbiological standards for drinking water quality (Edema et al., 2011; Singla et al., 2015). However, many emerging researches indicated that long-term consumption of low-mineralized water having low total dissolved solid (TDS), low hardness, and also low in certain nutrients may lead to increase in cardiovascular diseases and other health problems (Akpoborie and Ehwarimo, 2012).

The major supplier of PDW that has become very popular among the medium- and low-income group people are company sealed bottles and bubble top cans. With the increase in demand among common people many small entrepreneurs, other than renowned company, launched PDW business. In order to access the quality of PDW, water quality index (WQI) is considered one of best effective way to describe water quality. Moreover, physicochemical and bacteriological parameters are compared with respect to acceptable limit as per IS 10500 (2012), IS 14543 (2004), and international (WHO, IBWA, USFDA, and USEPA) standards (IBWA, 2012). The PDW being soft and with low minerals (e.g., calcium, magnesium, and fluoride), its long-term consumption may lead to increase in cardiovascular diseases and other health problems. Both, manufactures and consumers should be aware of this.

Our study recommends regular monitoring and survey by concerned government authority about quality control of PDW. On the other hand, KMC water supply showed quite higher results satisfying the said standards.

The study reflected that RO filters converted all effluent water into excellent category, although 83% of these effluent showed pH value below 6.5 (acidic), which cannot be relaxed as per the BIS. The study also showed the overall performance of RO filters with respect to removal percentage of different minerals and hardness is substantially high and after filtration the water is converted to soft to moderate hard, which may lead to increase in cardiovascular diseases and other health problems on long-term consumption.

In the case of other built-in stand-alone filters, this study showed that turbidity removal have been 12%–99% with an average of about 71%, which may be considered as good efficiencies but for other criteria [TDS, total hardness (TH), Cl^-, and F), the removal efficiencies are very low.

Regarding performance of ceramic candle filters, this study showed that candle filters can remove about 67% of coliform bacteria. On average, it can remove >99% turbidity, but TDS and hardness removal efficiencies are negligible. In the effluent water mild increment in pH has been observed (4%–6%). Also a nominal enhancement of chloride and fluoride has been found.

3.2 Study Area

The Kolkata Municipal Area and its surrounding areas in West Bengal have been identified as study area. Kolkata city lies on longitude 88°24′E of Greenwich meridian and latitude 22°32′N of the Equator and located on the east bank of river Hooghly. In addition to being the largest indigenous city in West Bengal, this is an important trade, educational, and cultural center of Eastern India. Many industries are established in and around Kolkata city. The total area covered by the city is 185 km^2. The metropolitan region of the city covers an area of 1886.67 km^2. According to the census conducted in 2011, the population of the city is about 45 lakh, making it the seventh most populated city in India. The metropolitan region of the city houses a population of >141 lakh and the metropolitan region of the city is ranked as the third most populated metropolitan region of the country. The density of population of Kolkata is 24,250/km^2. The use of PDW is increasing day by day in Kolkata city and its surrounding metropolitan areas. At the same time the usage of different types of domestic water purifiers (RO type, normal stand-alone type) has also increased at houses, offices, and institution because of more awareness among people. All these samples of water were collected from north metropolitan areas to south and east metropolitan area to west. Some of the locations are Kalyani, Salt Lake, Bidhannagar, Sealdah, Esplanade areas, Howrah station, Madhyamgram, Baruipur, Behala, Bhowanipur, Gariahat, and Jadavpur areas. Candle filters were purchased from different markets in Kolkata and used to filter samples of borehole (BH) water and KMC supply water collected from two locations. Besides, some samples were prepared by KMC water mixed with sewage and mud and get it filtered through candle filter to find out its performance.

3.3 Objectives

The objectives of the present study are as follows:

1. To assess the status of water quality of PDW, manufactured and sold by many companies and vendors in Kolkata city.
2. To compare obtained water quality parameters of the PDW with the specifications as per "IS-10500 (2012) for Drinking Water Specifications" as well as "IS:14543 (2004) for Package Drinking Water Specifications." To evaluate the performance of different types of water purifiers such as RO filter, built-in stand-alone filter, and normal candle filter of various make and manufacture.

3.4 Materials and Methods

In the study, 27 types of bottled PDW and 10 types of bubble top can PDW of various brands were analyzed. Plastic containers used for

PDW were food grade quality. Physicochemical and bacteriological parameters of the collected samples were analyzed at School of Water Resources Engineering, Jadavpur University as per procedure prescribed by APHA (2012) guidelines. Further, 18 samples of KMC supply water, collected randomly from different locations of Kolkata, were analyzed and the results were compared with that of PDW. At first, the samples were tested for bacteriological parameter such as total coliform with H_2S strip method. Thereafter, physicochemical analysis was carried out for eight different water quality parameters as per standard methods (APHA, 2012). The parameters included pH, turbidity, TDS, TH, calcium (Ca), magnesium (Mg), chloride (Cl^-), and fluoride (F^-). The pH and turbidity were measured using digital pH meter and nephelo-turbidity meter, respectively. The TDS was measured with digital TDS meter, whereas F^- was determined with ion meter using ion-selective electrode (ISE). The TH was determined with EDTA titration method and Cl^- was determined with argentometric method using potassium chromate solution as indicator and standard silver nitrate solution as titrant (Ray et al., 2016).

3.5 Methodology of the Work

3.5.1 Collection of Sample

PDW—bottled water: The samples of bottled water of different brands were collected from various key locations at Kolkata city.

PDW—bubble top cans: The samples of water were collected through polyethylene bottles from different social ceremonies/occasions, etc., at Kolkata.

The following information were noted for the above-mentioned methodologies:

1. sample no.
2. date of collection
3. location from where the sample were collected
4. name of the brand
5. name of the manufacturer
6. date of packaging
7. batch no.

Drinking water obtained from purifiers (RO purifiers and normal built-in wall mounted stand-alone purifiers): The samples of water were collected in polyethylene bottles from different offices, institutions, and residential houses in Kolkata and surrounding areas. In this case, two samples for each purifier, that is, one from inlet before filtration and other from outlet after filtration were collected. During the sample collection following points were noted:

1. filter no.
2. name of filter/purifier with company name

3. inlet sample no. (before filtration)
4. outlet sample no. (after filtration)
5. date of sample collection
6. source of water filtered (KMC supply/municipal supply/BH water)
7. name of office/institution/residence from where the sample collected
8. location of the office/institution/residence

Drinking water obtained from stand-alone candle filter fixed in cylindrical container: The samples of water were collected in polyethylene bottles from stand-alone candle filter of different manufactures from residence in Kolkata and surrounding areas. In this case also, two samples of water for each filter, that is, one before filtration and other after filtration were collected. During the sample collection the following points were noted:

1. filter no.
2. name of filter/purifier candle with company name
3. prefilter sample no. (before filtration)
4. postfilter sample no. (after filtration)
5. date of sample collection
6. source of water filtered (KMC supply/municipal supply/BH water)
7. name of residence from where the sample were collected
8. location of the residence

3.5.2 Testing of Sample

In all the above cases, after sample collection, immediately the same was tested for the presence of total coliform/bacteria by total coliform detection kit/bacteria detection kit (H_2S strip). The result in this process indicates whether total coliform is present or not.

At the same time, the samples were analyzed for physiochemical test for different parameters, that is, pH, turbidity, TDS, TH, chloride, and fluoride as per procedure laid down in APHA (2012).

3.6 Results and Discussion

3.6.1 Bottled Package Drinking Water (Ray, 2015; Ray et al., 2016)

In the case of bottled PDW, water samples of 27 brands were tested in laboratory for the determination of each of the seven water quality parameters (i.e., presence of coliform bacteria, pH, Turbidity, TDS, TH, chloride, and fluoride). Then the WQI was calculated and it is observed that all the water samples (100%) fell under excellent category

(WQI <50) and average WQI value was 20. The detailed results, analysis thereof, comparisons of seven parameters with respect to that as stipulated in IS 10500 (2012) (Drinking water specification) and IS 14543 (2004) [PDW (other than natural mineral water) specification] have been done. The results are as follows:

Coliform bacteria: No samples were found to have the presence of coliform organism, which indicate safe for drinking.

pH: In all 41% samples had pH values below 6.5, which does not conform to IS 10500 (2012) (drinking water specification) and IS 14543 (2004) [PDW (other than natural mineral water) specification]. These values indicate that these proportions of PDW (bottled) are acidic. Balance 59% of samples had pH between 6.5 and 8.5 conforming to the above-mentioned IS codes. The below ranged pH value (<6.5) may be due to conversion of dissolved CO_2 to carbonic acid which is generally obtained after filtered by RO purifiers. From these results it can be assumed that all these PDW might have been manufactured through RO water filters.

Turbidity: All the samples were found to have turbidity within the acceptable limit (<1 NTU) as per aforesaid codes. In all 48% samples had turbidity below 0.1 NTU and balance 52% has turbidity between 0.1 and 0.2.

TDS: All the samples were found to have TDS within the acceptable limit (500 mg/L) as per aforesaid IS codes. In all 30% samples had TDS below 25 mg/L, 48% samples had TDS between 25 and 50 mg/L, 19% samples had TDS between 50 and 100 mg/L, and balance 3% had TDS >100 mg/L.

About 78% samples contained TDS below 50 mg/L (very low mineral concentration; <50 mg/L, Ref. EU mineral water directive) and 22% samples contained TDS between 50 and 120 mg/L (low mineral concentration, TDS 50–500 mg/L). Average TDS were 38.26 mg/L.

TH: Similarly, all the samples were also found to have hardness much below the acceptable limit (200 mg/L) as per IS 10500. Here, 78% samples had TH below 25 mg/L, 15% samples had TH between 25 and 50 mg/L, and balance 7% had TH between 50 and 100 mg/L.

Between 93% and 7% samples showed TH below 50 mg/L (soft water) and 50–100 mg/L (moderate hard water), respectively. Average TH was calculated to be 17.58 mg/L.

Chloride: All the samples were found to have Cl^- within the acceptable limit (200 mg/L) as per IS 14543 (2004). About 89% samples had Cl^- below 20 mg/L, 7% samples had Cl^- between 20 and 40 mg/L, and balance 4% samples showed Cl^- between 40 and 60 mg/L.

Fluoride: All the samples were found to have F^- within the acceptable limit (1 mg/L) as per IS 14543 (2004). About 85% samples found F^- below detectable level (BLD) and the balance 15% samples showed F^- within 0.02 mg/L, which is far below the acceptable limit.

3.6.2 Bubble Top Can Package Drinking Water

In the case of bubble top can PDW, water samples of 10 brands were tested in laboratory for the determination of each of the seven water quality parameters (i.e., presence of coliform bacteria, pH, turbidity, TDS, TH, chloride, and fluoride). Based on the result, the WQI has been worked out. On the basis of the WQI values, it is also found that all the water samples (100%) lie under excellent category (WQI <50) and average WQI was 19. Besides the following findings have also been observed:

Coliform bacteria: No samples were found to have presence of coliform organism, which indicate safe for drinking so far microbiological parameter is concerned.

pH: About 90% samples were found to have pH values below 6.5, which does not conform to IS 10500 (2012) (drinking water specification) and IS 14543 (2004) [PDW (other than natural mineral water) specification]. This value indicates that this proportion of bubble top can PDW is acidic. Balance 10% samples have pH between 6.5 and 8.5 conforming to the above-mentioned IS codes. The below ranged pH value (<6.5) may be due to conversion of dissolved CO_2 to carbonic acid which is generally obtained after being filtered by RO purifiers. From these results it can be assumed that all these PDW might have been manufactured through RO water filters.

Turbidity: All samples were found to have turbidity within the acceptable limit (<1 NTU) conforming to aforesaid codes. Here, 10% samples have turbidity below 0.1 NTU while 50% have turbidity between 0.1 and 0.2 and balance 40% samples have turbidity >0.2 NTU with a maximum value of 0.31.

TDS: All samples were found to have TDS within the acceptable limit (500 mg/L) as per aforesaid IS codes. In this case, 50% samples have TDS below 25 mg/L, and balance 50% samples have TDS between 25 and 50 mg/L.

However, all samples (100%) contained TDS below 50 mg/L (very low mineral concentration; <50 mg/L, Ref. EU mineral water directive) and average TDS were 24.68 mg/L.

TH: In this case, all samples were found to have hardness within the acceptable limit (200 mg/L) as per IS 10500. Here, 70% samples have TH below 25 mg/L, other 30% samples have TH between 25 and 50 mg/L with a maximum value of 32 mg/L.

That is, all samples (100%) showed TH below 50 mg/L (soft water) with average value of 21.20 mg/L.

Chloride: All samples were found to have Cl^- much below the acceptable limit (200 mg/L) as per IS 14543 (2004). About 80% samples have Cl^- below 20 mg/L, and balance 20% samples have Cl^- between 20 and 40 mg/L with a maximum value of 36 mg/L.

Fluoride: All samples were found to have F^- within the acceptable limit (1 mg/L) as per IS 14543 (2004). About 90% samples were found F^- as BDL and the balance 10% samples showed F^- within 0.02 mg/L, which is far below the acceptable limit.

3.6.3 Reverse Osmosis (RO) Water Filter

A total of six domestic RO filters of different make and manufacture were arbitrarily chosen from different locations of Kolkata. For each RO filter, two water samples were collected, that is, one before entering into the filter (prefilter) and other after filtration (postfiltered drinking water). Thus a total of 12 water samples were tested in the laboratory for the determination of each of the seven water quality parameters (i.e., presence of coliform bacteria, pH, turbidity, TDS, TH, chloride, and fluoride).

Based on the result, the WQI of all the samples has been worked out. On the basis of the WQI values, it was observed that WQI of prefiltered water varied from 163 (poor category) to 34 (excellent category), whereas WQI of all the postfiltered water (i.e., 100% samples) varied from 27 to 16 which fell under excellent category (WQI < 50). The detailed results, analysis thereof, comparisons of seven parameters with respect to the acceptable values as stipulated in IS 10500 (2012) (Drinking water specification) have been carried out, which were shown (Analysis of Results) in tabulated form, graphical representation, etc. In addition to these, following findings have also been observed:

Coliform bacteria: No samples, either prefiltered or postfiltered drinking water, were found to have the presence of coliform organism, which indicates safe for drinking as per microbiological parameter's point of view.

pH: All prefiltered water samples had *pH* values from 7.36 to 7.79 (average 7.60), which was within the acceptable limit (6.5–8.5) as per IS 10500 (2012).

After filtration by RO filter, *pH* values found ranging from 5.61 to 7.15 (average 6.11). It showed that all 83% filtered water samples have pH values below 6.5 and acidic in nature, which does not conform to IS 10500 (2012). Balance 17% samples had pH between 6.5 and 8.5 conforming to the code. The below ranged pH value (<6.5) may be due to conversion of dissolved CO_2 to carbonic acid which is generally obtained after filtered by RO purifiers.

Turbidity: In prefiltered water, 33% samples had turbidity more than acceptable limit (1 NTU) and in postfiltered water, 100% samples showed turbidity within acceptable limit (<1 NTU).

In prefiltered water, 17% samples had turbidity <0.1 NTU, 50% samples had turbidity between 0.2 and 0.4 NTU, and balance 33% samples had turbidity >0.4 NTU with a maximum value of 3.38. Average turbidity was 0.97 NTU.

In contrast after filtration all samples (100%) have achieved the turbidity below 0.20 NTU. Average turbidity of postfiltered water by RO filter has been found to be 0.13 NTU.

Percentage removal of turbidity varied from 27% to 98%, that is, an average removal of about 62%.

TDS: In prefiltered water, 66% samples had TDS within acceptable limit (500 mg/L), out of which 33% samples had TDS between 100 and 200 mg/L and 33% samples had TDS between 300 and 500 mg/L. Balance 34% samples had TDS above 500 mg/L (i.e., between 1000 and 1260 mg/L).

In the case of postfiltered water, all samples were found to have TDS between 6.9 and 108 mg/L. Out of this 67% samples had TDS <100 mg/L.

Percentage removal of TDS varied from 65% to 97%, with an average removal of around 89%.

TH: In prefiltered water, 67% samples had TH within acceptable limit (200 mg/L), and between 100 and 200 mg/L. Balance 33% samples had TH above 200 mg/L (i.e., between 300 and 600 mg/L). In the case of postfiltered water, all samples were found to have TH between 12 and 72 mg/L. Out of this 67% samples had TDS <50 mg/L.

Percentage removal of TH varied from 49% to 96%, with an average removal of around 82%.

Chloride: In prefiltered water, 67% samples had chloride (Cl^-) within acceptable limit (250 mg/L), out of which 33% samples had Cl^- below 50 mg/L, 17% samples had Cl^- between 50 and 150 mg/L, and 17% samples had Cl^- between 150 and 250 mg/L. Balance 33% samples had Cl^- above 250 mg/L (i.e., between 400 and 610 mg/L).

In the case of postfiltered water, all samples were found to have Cl^- between 5 and 52 mg/L. Out of this 83% samples had Cl^- <50 mg/L.

Percentage removal of Cl^- varied from 32% to 91%, with an average removal of around 80%.

Fluoride: In prefiltered water, all samples (100%) had fluoride (F) within acceptable limit (1 mg/L), out of which 50% samples had F between 0.10 and 0.3 mg/L, 17% samples between 0.30 and 0.5 mg/L and balance 33% samples had F >0.5 mg/L (i.e., between 0.5 and 0.65 mg/L).

In the case of postfiltered water, all samples were found to have F below 0.076 mg/L. Out of this 67% samples showed F as BDL. Percentage removal of F varied from 60% to 100%, with an average removal of around 93%.

3.6.4 Domestic Built-In Stand-Alone Filters

A total of 20 normal built-in filters (stand-alone) of different make and manufacture were arbitrarily considered from different domestic residences and offices in and around Kolkata city. Out of the 20 filters, 6 were used for BH water filtration, 1 for mixed water, and 13 filters for filtration of KMC supply water. For each filter, two water samples were collected, that is, one before entering into the filter (prefilter) and other after filtration (postfiltered drinking water). Thus a total of 40 water samples were tested in laboratory for the determination of seven water quality parameters as mentioned earlier.

Based on the result, the WQI of all the samples have been calculated. Based on the WQI values, it has been observed that

- WQI of prefiltered water varied from 122 (poor category) to 33 (excellent category), whereas WQI of 19 postfiltered water (i.e., 95% sample) varied from 118 (poor category) to 29 (excellent category).
- In prefiltered water 12 samples (60%) were excellent (WQI <50), while in postfiltered water 13 samples (65%) were found to be excellent.
- In prefiltered water two samples (10%) were good (WQI: 50–75), whereas in postfiltered water four samples (20%) were found to be good.
- In prefiltered water two samples (10%) were fair (WQI: 75–100), whereas in postfiltered water one sample (5%) was found to be good.
- In prefiltered water four samples (20%) were poor (WQI: 100–200), whereas in postfiltered water one sample (5%) was found to be good and balance one sample found to be unsuitable (WQI >300) due to the presence of coliform bacteria.

The detailed results, analysis thereof, comparisons of seven parameters with respect to the acceptable values as stipulated in IS 10500 (2012) (drinking water specification) have been carried out, which were shown (Analysis of Results) through tabulated form, graphical representation, etc. In addition to these, following findings have also been observed:

Coliform bacteria: No prefiltered samples of water were found to have the presence of coliform organism, which indicate safe for drinking as per microbiological parameter's point of view. In the case of postfiltered water, one sample indicated the presence of coliform bacteria, which may be due to noncleaning of filter and its candle for a long time.

pH: All prefiltered water samples had *pH* values from 6.85 to 7.82 (average 7.51), which is within the acceptable limit (6.5–8.5) as per IS 10500 (2012). On the other hand, *pH* of all postfiltered water varied from 6.90 to 7.76 (average 7.48). From this result, it can be found that normal stand-alone, built-in domestic filter cannot make any remarkable change in pH unlike RO filters.

Turbidity: In prefiltered water, 60% samples were found to have turbidity within the acceptable limit (<1 NTU), 35% samples had turbidity between 1 and 5 NTU (permissible limit, in the absence of alternate source), and 5% samples had turbidity >5 NTU. In the case of postfiltered water, 100% samples were found to have turbidity within acceptable limit (<1 NTU), having a maximum value of 0.44 NTU.

In prefiltered water, 5% samples had turbidity between 0.2 and 0.4 NTU, 30% samples had turbidity between 0.4 and 0.6 NTU, 25% samples had turbidity between 0.6 and 1.0 NTU, and balance 40% samples had turbidity >1.0 NTU with a maximum value of 5.64. Average turbidity was 1.24 NTU.

In contrast after filtration 50% samples have achieved turbidity below 0.20 NTU, 40% samples had between 0.2 and 0.4 NTU, and balance 10% samples had turbidity between 0.4 and 0.6 NTU with a maximum value of 0.44 NTU. Average turbidity was 0.22 NTU.

Percentage removal of turbidity varied from 12% to 99%, having an average removal of about 71%.

TDS: In prefiltered water, 80% samples had TDS within acceptable limit (500 mg/L) and balance 20% water had TDS between 500 and 1050 mg/L (permissible limit: 2000 mg/L, in the absence of alternate source). After filtration this status remained unchanged.

Percentage removal of TDS varied from 0% to 40%. Moreover, TDS gain (1%–20%) has been observed in some postfiltered water samples, which may be due to leaching of candle materials. Overall average TDS removal was calculated to be around 5%.

TH: In prefiltered water, 65% samples had TH between 100 and 200 mg/L, which is within the acceptable limit (200 mg/L), 30% samples had TH between 200 and 600 mg/L (permissible limit), and balance 5% samples had TH >600 mg/L (max 676 mg/L).

In the case of postfiltered water, 55% samples had TH between 100 and 200 mg/L, which is within the acceptable limit (200 mg/L), 40% samples had TH between 200 and 600 mg/L (permissible limit), and balance 5% samples had TH 600 mg/L (max 660 mg/L).

Percentage removal of TH varied from 0% to 30%. Moreover, TH gain (1%–18%) has been observed in some postfiltered water samples, which may be due to leaching of candle materials. Overall average TDS removal was calculated to be around 8%.

Chloride: In prefiltered water, 85% samples showed chloride (Cl^-) concentration within acceptable limit (250 mg/L) and 15% samples have chloride (Cl^-) concentration between 250 and 1000 mg/L (permissible limit). After filtration this status remained unchanged.

In the case of prefiltered samples, 55% samples had Cl^- <50 mg/L, 25% samples had Cl^- concentration 50–150 mg/L, 5% samples had Cl^- concentration 150–250 mg/L, and balance 15 had the value range between 250 and 1000 mg/L with a maximum value of 539 mg/L.

For postfiltered samples, these status changed a little bit. Here 60% samples had Cl^- <50 mg/L, 20% samples had Cl^- concentration 50–150 mg/L, 5% samples had Cl^- concentration 150–250 mg/L, and balance 15% had the value range between 250 and 1000 mg/L with a maximum value of 522 mg/L.

Percentage removal of Cl^- varied from 0% to 44%, with an average removal percentage of around 17%. Here also chloride gain at the rate 14% occurred in one (5%) sample. The result indicates a lower performance of filter with respect to chloride removal.

Fluoride: In prefiltered water, all the samples (100%) found to have fluoride (F) within acceptable limit (1 mg/L), and obviously all postfiltered water showed the concentration within the limit. Here, in all the study samples, F^- were found to range from 0.098 mg/L to 0.526 mg/L in prefiltered water, whereas the same observed to be in the range 0.1–0.518 mg/L in filtered water samples.

Percentage removal of F^- varied from 0% to 13%, with an average removal of around 5%. For some samples fluoride addition at 1%–8% has been detected, which may be due to leaching of fluoride from candle materials.

From the above results, it is found that turbidity removal efficiency of built-in normal filters (stand-alone) is very good but removal efficiencies of other criteria are not substantial like RO filters.

3.6.5 KMC Supply Water Filtered by Candle Filters

A total of 11 candle (ceramic) filters of different make have been considered in order to investigate their performances. Through these filters 15 water samples were passed for filtration out of which 2 were BH water and 13 were KMC supply water collected from domestic residences. For each filter, two water samples were collected that is, one before entering into the filter (prefilter) and other after filtration (postfiltered drinking water). Thus a total of 40 (forty) water samples were tested in the laboratory for the determination of seven water quality parameters as mentioned earlier.

Based on the observed results of seven parameters, the WQI of all the samples have been calculated. Based on the WQI values, it has been observed that

- WQI of prefiltered water mainly varied from 91 (fair category) to 41 (excellent category), except one sample was found to be unsuitable for drinking (WQI > 300) due to the presence of coliform bacteria. On the other hand, WQI of postfiltered water varied from 75 (good category) to 35 (excellent category).
- In prefiltered water, 12 samples (80%) were excellent (WQI < 50), while in postfiltered water 13 samples (87%) were found to be excellent.
- In prefiltered water, two samples (13%) were fair (WQI: 75–100), which turned to good quality (WQI: 50–75) after filtration.

- In prefiltered water, in one sample (7%), bacteria were detected, which converted to excellent category after filtering, that is, it removed coliform bacteria.

The detailed results, analysis thereof, comparisons of seven parameters with respect to the acceptable values as stipulated in IS 10500 (2012) (drinking water specification) have been carried out, which were shown (Analysis of Results) through tabulated form, graphical representation, etc. In addition to these, following findings have also been observed:

Coliform bacteria: Only one prefiltered sample of water of KMC supply was found to have the presence of coliform organism, which was removed by filtration. Balance 19 prefiltered samples did not show the presence of coliform bacteria, which indicates safe for drinking as per microbiological parameter's point of view. In the case postfiltered water, no bacteria was detected in the entire samples.

pH: All prefiltered water samples had *pH* values from 7.49 to 7.85 (average 7.64), which is within the acceptable limit (6.5–8.5) as per IS 10500 (2012). On the other hand, *pH* of all postfiltered water varied from 7.55 to 8.84 (average 7.95).

It was observed that most candle filters increased the pH values after filtration and here two samples (13%) showed *pH* above acceptable limit (>8.5). This has happened because new filters were used after 2 days use, resulting in leaching of carbonate, bicarbonate, and other salts from candle materials and dissolved in filtered water and became alkaline.

Turbidity: In prefiltered water, 80% samples were found to have turbidity within the acceptable limit (<1 NTU) and 20% samples had turbidity between 1 and 5 NTU (permissible limit, in the absence of alternate source). In the case of postfiltered water, 93% samples were found to have turbidity within the acceptable limit (<1 NTU) and 7% samples had turbidity below 5 NTU (1.76 NTU).

In prefiltered water, 60% samples had turbidity between 0.4 and 0.6 NTU, 20% samples had turbidity between 0.6 and 1.0 NTU, and balance 20% samples had turbidity >1.0 NTU with a maximum value of 3.83. Average turbidity was 1.01 NTU.

In contrast after filtration 50% samples have achieved the turbidity below 0.20 NTU, 33% samples had between 0.2 and 0.4 NTU, 7% samples had between 0.4 and 0.6 NTU, and balance 7% samples had turbidity >1.0 NTU with a maximum value of 1.76 NTU. Average turbidity was 0.31 NTU.

Percentage removal of turbidity varied from 29% to 96%, having an average removal efficiency of about 64%.

TDS: In prefiltered water, 100% samples had TDS within acceptable limit (500 mg/L). After filtration this status remained the same.

In prefiltered water, 7% samples had TDSs between 100 and 200 mg/L, 80% samples had TDS between 200 and 300 mg/L, and balance 13% samples had TDS between 300 and 500 mg/L (max 462 mg/L).

In postfiltered water, 14% samples had TDSs between 100 and 200 mg/L, 73% samples had TDS between 200 and 300 mg/L, and balance 13% samples had TDS between 300 and 500 mg/L (max 462 mg/L).

Percentage removal of TDS varied from 0% to 18%. It was also observed that about 47% samples showed enhanced TDS (1%–22%), due to leaching of different salts from candle materials. As such, on the whole average TDS removal was found to be negligible.

TH: In prefiltered water, 80% samples had TH between 100 and 200 mg/L, which is within the acceptable limit (200 mg/L) and balance 20% samples had TH between 200 and 600 mg/L (permissible limit) having maximum value of 328 mg/L. Here also, after filtration this status remained unaltered.

Percentage removal of TH varied from 3% to 24%. Moreover TH gain (2%–18%) has been observed in 53% postfiltered water samples, because of leaching of salts from candle materials. As such, on the whole average TDS removal was found to be negligible.

Chloride: In prefiltered water, all samples (100%) showed chloride (Cl^-) concentration within acceptable limit (250 mg/L). After filtration this status remained unchanged.

In the case of prefiltered samples 13% samples had $Cl^- <50$ mg/L and balance 87% samples had Cl^- concentration in the range 50–150 mg/L with a maximum value of 130 mg/L.

For postfiltered samples these status changed a little bit. Here 7% samples had $Cl^- <50$ mg/L, and balance 93% samples had the Cl^- concentration between 50 and 150 mg/L with a maximum value of 129 mg/L.

Percentage removal of Cl^- varied from 1% to 25%. Moreover, Cl^- gain (3%–39%) has been observed in 33% postfiltered water samples, because of leaching of salts from candle materials. As such, on the whole average Cl^- removal performances were found to be negligible, rather overall gain of TDS was calculated to be around 2%.

Fluoride: In prefiltered water, all samples (100%) were found to have fluoride (F) within acceptable limit (1 mg/L), and obviously all postfiltered water showed the concentration within the limit. Here, in all the studied samples, F^- were found to be in the range 0.109–0.254 mg/L in prefiltered water, whereas the same was observed to be in the range 0.144–0.365 mg/L in filtered water samples.

It is observed that most of the candles (73%) have added F^- after filtration instead of removal and average addition is worked out to be about 16%. These phenomena occurred due to leaching of fluoride from candle materials.

From the above results, it can be found that except turbidity removal, the efficiencies of candle filters were very negligible toward the removal of other physiochemical criteria such as TDS, pH, TH, chloride, and fluoride. The concentration of these parameters remained almost same after filter, rather concentration of few parameters have increased due to leaching of different salts from ceramic candles.

As cited above, only one prefiltered sample was traced with coliform bacteria, which was effectively filtered by the candle. All other samples, both prefiltered and postfiltered, were found to be free from coliform bacteria. Overall WQI of all the prefiltered samples was perfectly alright except the one in which coliform organism was present. Thus, it can be seen that overall performance and efficiency of candle filters obtained hereinabove based on filtration were mostly safe and good, the sources of which were either KMC supply or BH water.

In view of the above, it was felt to examine some prepared water samples with the same candles of different make for better assessment of candle-filter performances and efficiencies. Accordingly, nine samples were prepared by mixing some clay and sewage water with KMC supply water. Sewage and clay were mixed to add the coliform bacteria and turbidity, TDS, etc. respectively.

Thereafter, laboratory examination was carried out for the determination of all seven water quality parameters as before toward all prefiltered and corresponding postfiltered water samples. A total of 18 samples were tested for nine candles under consideration.

3.6.6 Prepared Water Sample (as Controlled) Filtered by Candle Filters

Based on the observed results of seven parameters, the WQI of all the samples have been calculated. Based on the WQI values, it was observed that

- WQI of all prefiltered water samples was very high mainly due to the presence of bacteria and very high turbidity. Obviously all the prepared samples were not suitable for drinking because of its very high turbidity, coliform bacteria, color, odor, etc. It may once again be mentioned that the WQI has been calculated based on the seven parameters only, in this study.
- It was found that 55% postfiltered samples converted to excellent category (WQI <50), 11% samples converted to good category (WQI: 50–75), and balance 34% postfiltered samples found to be unsuitable for drinking, which is mainly due to presence of coliform bacteria.

The detailed results, analysis thereof, comparisons of seven parameters with respect to the acceptable values as stipulated in IS 10500 (2012) (drinking water specification) have been carried out. The following findings have also been observed:

Coliform bacteria: All nine (100%) prefiltered samples, which were prepared actually, contained total coliform bacteria. After filtration by candle filters, six (67%) samples showed absence of bacteria while rest 33% indicated the presence of the bacteria. It implied that about 67% candle filters could remove coliform bacteria during filtration.

pH: All prefiltered water samples had *pH* values from 7.05 to 7.33 (average 7.18), which is within the acceptable limit (6.5–8.5) as per IS 10500 (2012). On the other hand, *pH* of all postfiltered water samples varied from 7.40 to 7.88 (average 7.63).

As previously noted, it was also observed that all candle filters increased the *pH* values after filtration and here all samples showed *pH* within acceptable limit (6.5–8.5).

Turbidity: Owing to mixing of clay, mud, and sewage water with prefiltered water samples, the turbidity became very high. During test, turbidity obtained was in the range 379–982 NTU. In postfiltered water samples, 67% samples' turbidity came down to the range of 0.31–0.77 NTU, which were within the acceptable limit (<1 NTU), and balance 33% samples had turbidity below 5 NTU (max 2.46 NTU).

After filtration 22% samples had turbidity between 0.2 and 0.4 NTU, 12% samples had between 0.4 and 0.6 NTU, 33% samples had between 0.6 and 1.0 NTU, and balance 33% samples had turbidity >1.0 NTU with a maximum value of 2.46 NTU. Average turbidity was calculated to be 0.99 NTU.

For all the candles, percentage removal efficiency of turbidity has been found >99%, with an average of 99.85%.

TDS: In prefiltered water, 100% samples were found to have TDS within acceptable limit (500 mg/L). After filtration this status remained unchanged. From this TDS result, it is evident that practically no dissolved solid has been added with water after mixing mud soil and sewage water. Only suspended solids and colloidal materials were responsible for very high turbidity of the prepared samples.

In prefiltered water, 22% samples had TDSs between 100 and 200 mg/L and 78% samples had TDS between 200 and 300 mg/L (max 279 mg/L).

In postfiltered water, 33% samples had TDSs between 100 and 200 mg/L and 67% samples had TDS between 200 and 300 mg/L (max 264 mg/L).

Percentage removal of TDS varied from 3% to 17%. It was also observed that about 33% postfiltered samples showed enhanced TDS (18–26%), due to leaching of different salts from candle materials. As such, on the whole average TDS removal was found to be negligible. As shown earlier, the same findings were observed in the case of filtration of KMC supply/BH water.

TH: In prefiltered water, 89% samples had TH between 100 and 200 mg/L, which is within the acceptable limit (200 mg/L) and balance 11% samples had TH between 200 and 600 mg/L (permissible limit) having maximum value of 212 mg/L. After filter, in 100% samples TH was found to be between 100 and 200 mg/L.

Percentage removal of TH varied from 8% to 26%. Moreover, TH gain (2%–16%) has been observed in 66% postfiltered water samples, because of leaching of salts from candle materials. As such, on the whole average TDS removal was found to be negligible.

Chloride: In prefiltered water, all samples (100%) showed chloride (Cl^-) concentration within acceptable limit (250 mg/L). After filtration this status remained unchanged. The same findings were observed in the case of KMC water samples.

In the case of prefiltered water, 89% samples had Cl^- concentration in the range 50–150 mg/L and balance 11% samples had the value >150 mg/L with a maximum value of 155 mg/L.

For postfiltered samples, these status changed a little bit. Here, 100% samples' Cl^- concentration found to be between 50 and 150 mg/L with a maximum value of 81 mg/L.

Percentage removal of Cl^- varied from 30 to 57. Overall average Cl^- removal performances was found to be around 42%.

Fluoride: In prefiltered water, all samples (100%) were found to have fluoride (F) within the acceptable limit (1 mg/L), and obviously all postfiltered water showed the concentration within the limit. Here, in all study samples, F^- were found to be in the range of 0.234–0.703 mg/L in prefiltered water, whereas, the same was observed to be in the range 0.233–0.603 mg/L in filtered water samples.

Percentage removal of F^- varied from 4% to 44%. In some cases, F^- addition has taken place. Overall, 9% F^- removal has taken place.

From the above results, it is evident that due to the mixing of clay mud and sewage water with drinking water, it did not contribute to add TDS, TH, chloride, and fluoride. The parameters such as turbidity, pH, and bacteriological parameters were changed significantly.

The above observations and comparison of results for both normal water samples (KMC supply/BH water) and artificially prepared samples, with respect to seven different water quality parameters, are depicted herein under for both prefiltered and postfiltered water, passed through different domestic built-in (stand-alone) filters, with the help of graphical representations, pi-diagrams, etc.

3.7 Conclusion

The major findings of this study suggest that 41% (bottled) to 90% (bubble top can) PDW have pH below 6.5, which cannot be relaxed as per BIS standard requirement and the performance RO filters with respect to removal percentage of different minerals and hardness is substantially high and after filtration the water converted to soft to moderate hard. The domestic stand-alone filters (built-in) are very good with respect to turbidity reduction efficiency but for other criteria (TDS, TH, Cl^-, and F), the removal efficiencies were very low. The efficiencies of ceramic candle filters (Ray, 2015; Ray et al., 2016) were very negligible toward the removal of physiochemical criteria except turbidity removal. Water quality of KMC supply collected directly for drinking purpose showed that all the seven water quality parameters of the direct supply water did not contain coliform organism and overall water quality was excellent (WQI <50). Moreover, long-term consumption of waters with low minerals (e.g., calcium, magnesium, and fluoride) and soft waters may lead to increase in cardiovascular diseases and other health problems. Both, manufactures and consumers should be aware of this. The study recommends regular monitoring and survey by concerned government body for quality control of PDW.

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4

WATER PURIFICATION TECHNOLOGIES

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4.1 Need for Water Purification

Provision of safe drinking water is an elementary human necessity and an important human right, especially for maintaining good health. The earth planet contains about 70% of water reservoirs in form of oceans, sea, rivers, lakes, and underground streams even then, 1000 million people worldwide living without the availability of safe drinking water and it is also clear from the studies that about 50% of them are affected by health issues due to shortage of healthy drinking water. People living in underdeveloped areas and in countries with poor economies usually drink water directly from rivers and ponds that resulted in fatal diseases like typhoid, diarrhea, cholera, hepatitis, polio, dysentery, and tapeworms (Werber et al., 2016). Data from selected countries on improved water resources in relation to life expectancy are shown in Table 4.1. This data indicates the chief expansion markers connected to water, fitness, and hygienic condition of seven dominated countries in the world that shows the significant differences between developing and developed countries. The table also presents very clearly that the children's health can be enhanced by the provision of good sanitation and safe drinking water. Availability of safe drinking water is directly correlated with better health in developed countries, about 99% population have good access to safe drinking water in developed countries like Spain or Norway, whereas in countries like Mozambique or Niger, the availability of safe drinking water finds to be less than 45%, so the birth success is very less in these countries and it is a fact that each year due to insufficient hygienic water, hygienic conditions, and sanitation deaths of about 1.5 million children are recorded. Not only this, more than 30% of children deaths has its roots in avoidable diseases that related to water and vulnerable deaths of about 90% among

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Table 4.1 Water Sanitation and Health Development Indicators

Rank's Position	Country	Human Development Index (HDI)	Life Expectancy at Birth (Years)	Under-Five Mortality Rate (per 1000 Live Births)	Population With Access to an Improved Sanitation (%)	Population With Access to an Improved Water Source (%)
1	Norway	0.965	79.6	4	100	100
8	United States	0.948	77.5	8	100	100
19	Spain	0.938	79.7	5	100	100
83	Ecuador	0.765	74.5	26	89	94
126	India	0.611	63.6	85	33	86
168	Mozambique	0.390	41.6	152	32	43
177	Niger	0.311	44.6	259	13	46

Source: Data extracted from Human Development Report; UNDP, 2006. United Nations Human Development Report. UNDP Press, USA.

the children under 5 years are recorded due to diarrheal diseases in the developing countries (Bain et al., 2014; Mehmood et al., 2013). Increased awareness of this problematic issue in previous years the population has highlighted the status of the basic need to safe and hygienic drinking water and to organize global attention for possible resolutions, as specified in numerous global statements such as 21 Program, UN Millennium Declaration in 2000 (Bain et al., 2014). State of World's Children in 2005 and the Human Development Report in 2006 were published and State Global Policy identifies that additional investigation for this ignored topic is required, and recalls that if water sanitation goals of the Millennium Development Goals are to meet in several emerging countries, the quantity of humans not having safe, clean, and hygienic water to drink must be halved by 2015. Water emergency in the developing nations should enforce to alleviate major health concerns in these countries. For this purpose, low-cost, ground-breaking, sustainable, and more effective technologies are required to provide safe drinking water to the consumer's treatment. A high level of skills is required in this area that will help to recover hygienic life style and the environment in underdeveloped countries (Khalid et al., 2014; Michalak et al., 2013).

There is a dire need to focus on water sources that are contaminated with human and animal wastes. Efforts should be made to treat these resources to reduce the risk of waterborne diseases. Engineering designs should be tailored in such a way to ensure safe limits of various physicochemical and microbiological parameters for raw water in available water resources. Different water treatment methods can be used to purify the water in these resources; some of the methods for purification are coagulation, flocculation, sedimentation, and chemical disinfection of raw water. But in the developing countries, these methods are highly variable in its use because of the availability of chemicals and resources (Bain et al., 2014). But some people mostly prefer to drink untreated water from the real and natural sources with some household water treatment methods like chlorination, boiling, etc. that are effective and low in cost.

4.2 Strategies in Water Management

Worldwide population has been increasing at fast pace, it becomes difficult to meet the full demand of water for growing population with the conventional methods and by existing processing methods of water. That is why the more conscientious use of the natural water resources, new and advanced strategies are required (WHO, 2011). Some of the strategies are summarized in Fig. 4.1.

Fig. 4.1 Management to protect water shortages and resources.

4.2.1 Production

This method is based to produce the safe drinking water from the saline and contaminated water to increase the amount of good quality drinking water and it must be obtained from the natural water reservoirs (WHO, 2011). Important strategies used in production procedures are stated as follows:

- removal of salts from the seawater by method of reverse osmosis (RO);
- separation of sulfates or by reducing the hardness components from hard water by nanofiltration (NF);
- water that received from dams and river sources purified by the method of ultrafiltration (UF).

4.2.2 Reuse

This method is created with a view to enhanced sanitization of wastewater by reprocessing of disinfected water which raises the exploitation possibility or decreases the safe drinking water, (WHO, 2011). Few examples are included:

- Discharged irrigation water can be reused by disinfecting the effluent by farm manure treatment machinery, using UF process to produce a good quality of water or with the help of membrane bioreactors.
- Clarification of gray water of hotel industry can be used in toilets and irrigation by using the UF.

- Backwash water can be used in swimming pools and for bathing purpose after sanitization by using the low-pressure RO.
- A huge amount of water can be collected during the process of backwashing of media filters at water plants and its reuse as potable water can be enhanced by using the UF.
- Clarification of gray type of water on ships can use practical graded water by UF technique and decontamination of pretreated industrial effluent in a semi-closed loop (UF, NF, low-pressure RO technique) for reprocessing.

4.2.3 Protections

This method is built on the inhibition of further adulteration in water reservoirs by enhanced decontamination of polluted and wastewater (WHO, 2011). Examples include landfill leachate sanitization and precise infiltration of the retentate to get landfill body which produces improved landfill gas which is quicker used in biodegradation process (NF and RO)

- acid mine drainage (AMD) handling by AMD NF;
- sanitization of waste products produced by animals, for example, pig slurry and dig estate through biogas plants using the techniques like UF, RO, nanofiltration;
- sanitization of the waste to decrease the adulteration of getting water contaminated by UF from sewage treatment plants; and
- sanitization of gray water present in different places like hotels or on ships can be done by techniques like membrane bioreactor based on UF process to protect the atmosphere.

Global concern is raised in recent times regarding ecological pollution, additional stringent lawful necessities regarding the quality related to regular use of water or drinking water, and stringent global waste release rules/guidelines. These are leading driving forces which increase the improved social acceptance and broader utilization/application of this knowledge in developing new techniques for water treatment (Vörösmarty et al., 2010). The alternative feature has been the cumulative understanding with regard to procedures connecting to the refusal linked features of the current technologies allowing for recovery of appreciated components, for example, the main goal of all water treatment strategies' is from wastewater discharge to clean water reuse. The idea behind water protection also applies to the clean water and it heightens the value of this precious commodity (water).

4.3 Technologies for Disinfection

A predominant goal for safe drinking water supply is the development of inexpensive and efficient technologies to provide wholesome water to the population. To achieve this goal, sterilization of water from traditional and developing pathogens is required without changing characteristics of water during the sanitization process. Most of the waterborne health problems are linked with the pathogens (Shannon et al., 2008). Mostly in the developing nations like sub-Saharan and southeast Asia, waterborne issues are responsible for the diseases like helminths, protozoa, fungi, viruses, and prions (Prüss et al., 2002). While some infectious agents eradicated or diminished, new ones continue to emerge and water is getting high importance in relation to the health of masses. Some filtration technologies are developing small units of filters along with ultraviolet (UV) radiation systems and ozonators to disinfect the water from microbes and are very important for water filtration plant developers.

4.3.1 UV Disinfection

Water purification is done using chemicals; UV lights are also effective for the inactivation of microorganisms. Germicidal wavelengths are used for the inactivation of protozoa, viruses, and bacteria (Song et al., 2016). The human naked eye cannot see this light. This light has shorter wavelengths as compared to visible light in the electromagnetic spectrum. Most of this light is absorbed by the earth ozone layer. A simple water treatment process using UV lights is shown in Fig. 4.2.

To be effective against microorganisms, the UV light should have a specific wavelength range, this limit is between the range of 200–300 nm are referred as germicidal which means that they have the ability to inactivating or distorting microorganisms, like bacteria, viruses, and protozoa (Lebik et al., 2014). This activity has permitted the use of UV light worldwide as an ecologically safe, chemicals free, and clean extremely real method of protection and sterilization of water against injurious microbes (Xu et al., 2013).

Although different chemical methods are available for the disinfection of water, UV radiation offers quick and most effective inactivation of microbial contamination through a physical procedure. When microorganisms are exposed to UV light it damages the DNA of the microorganism resulting in inactivation and growth retardation in the microbial population. UV irradiation has greater efficiency against all pathogenic microorganisms, including those organisms that are responsible for the spread of polio, cholera, hepatitis, typhoid, and other viral, bacterial, and parasitic diseases in drinking water. Along with this, UV irradiation has a weak activity for the transformation of chemical pollutants including pharmaceuticals, effluents from industry and pesticides by AOP (advance oxidation process) either alone or in addition with the use of H_2O_2 (hydrogen peroxide) (Song et al., 2016).

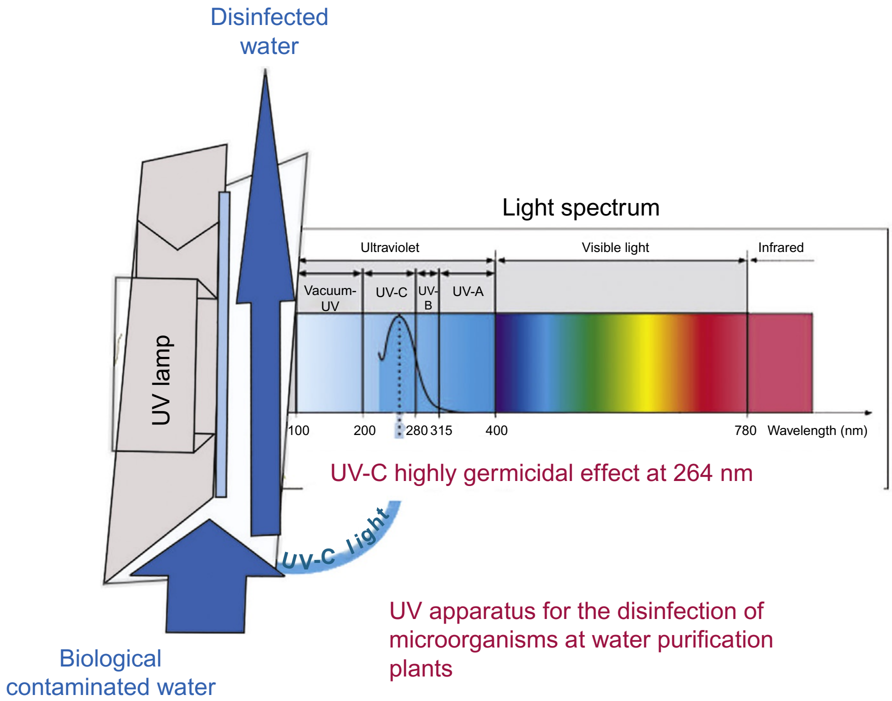

Fig. 4.2 An invisible ultraviolet light is a strong disinfectant for microorganisms.

Cellular RNA and DNA of the microorganisms absorb the high energy photons with the short wavelength at 254 nm (Santos et al., 2013). DNA dimers (linkages with the adjacent nucleotides forming double bonds) are produced by absorption of UV irradiation. Dimerization with adjacent molecules that is, nucleotide is the most prominent photochemical damage which may result in the formation of thymine dimmers as well. Formation of thymine dimmers in DNA is very important in the sense as these may inhibit replication of DNA of many pathogenic microorganisms (viruses or bacteria) and retards their growth so they may not be able to cause any infection (Strickler et al., 2015).

If the UV dose is low, some organisms may restore the photochemical mutation caused by UV irradiation via photo reactivation or dark repair. However, at amounts higher than 12 mJ/cm^2, experiments have illustrated that there is about the negligible potential for photoreactivation. It has also been noticed that few microbes like *Cryptosporidium* do not show any sign of nucleic acid that is, DNA repair under different conditions that is, light and the dark condition or pressure change like low-pressure or medium-pressure irradiation of

UV lamp at doses as low as 3 mJ/cm^2 (Santos et al., 2013). UV assembly should be designed keeping in view that it should deliver enough UV dose that should keep the cellular or photochemical damage and field testing should be performed to ensure the proper disinfection (Strickler et al., 2015).

There are various advantages of UV disinfection which are highlighted by Santos et al. (2013), Shannon et al. (2008), Song et al. (2016), and are listed as follows:

1. UV disinfection is a chemical-free method in which just light is pass out from the water.
2. UV light treatment does not require any storage, transportation, or exposure to dangerous/toxic chemicals.
3. UV lamp disinfection does not produce any lethal carcinogenic by-products which may affect the quality of the water adversely.
4. UV irradiation plays key role to inactivate the microorganisms including those pathogens which are resistant to chlorine like *Giardia* and *Cryptosporidium*.
5. UV light treatment may be utilized solely or in addition with H_2O_2 for decontamination of water for the removal of chemical pollutants and contaminants.

4.3.2 Ozonation

Ozone is a gas and it has specific properties like it is colorless and it has a distinctive odor, like the smell of the air after a thunderstorm (Xie et al., 2015). The use of ozone for water treatment in the United States and other countries was notable in 1800s. Ozone is a highly unstable and comprises three atoms of oxygen; due to instability the ozone molecule will quickly break down into oxygen and free radicals which have a very short life under normal conditions only survive for the milliseconds but these free radicals have a great reactivity potential (Ngwenya et al., 2013) (Fig. 4.3).

When compared with the chlorine, ozone has a much more tendency for the disinfection (Jiang et al., 2016). In addition, the oxidizing potential of ozone can also help to decrease the contamination of manganese, iron, and sulfur along with the elimination of taste and odor problems. The process of ozone reaction with sulfur contents and metals in the water may result in the production of elemental sulfur or insoluble metal oxides which can be eliminated by the employment of some measures at treatment facility after filtration (Richardson et al., 2000). During this process, other organic, inorganic contaminants and chemicals need to be clarified through either chemical oxidation or coagulation process. Ozone is an unbalanced element and its rate of dilapidation depends on the water chemistry, pH, and water temperature and ranges from few seconds to 30 min (Von Gunten, 2003).

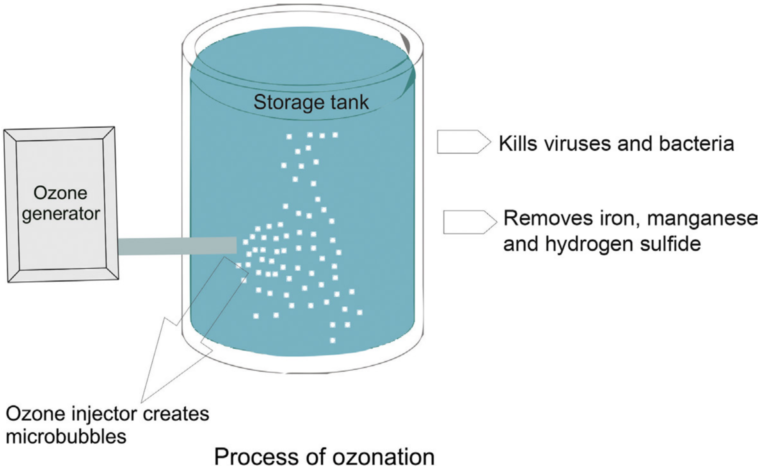

Fig. 4.3 Process of ozonation for water treatment.

4.3.2.1 Ozonation Process

Formation of ozone from oxygen is an energy consuming process. This process can be carried out in an instrument known as ozone generator and electric discharge is used to carry out this process for example, corona discharge (CD)-type ozone generators are available which produces ozone by utilizing a specific technique known as CD simulation of the lightning to produce ozone, and some ozone generators use UV radiations for the production of ozone as in UV-type ozone generators. Along with these profitable approaches process of ozone formation may also be completed through chemical reactions in conventional lab processes (Xie et al., 2015). The whole process involves a reaction in which clean and dry air are passed through a high-voltage electric discharge instrument commonly known as CD which breaks the molecules of oxygen and produces ozone molecules. Water treatment process leads approximately 1% or 10,000 mg/L absorption of ozone gas. UV ozonation is thought to be the best option for the small-scale systems while for the bulk production on a larger scale only the systems like CD and other massive generators for ozone production are considered as the favorable alternative (Richardson et al., 2000).

Raw water treatment is carried out by a process in which water is moved through a venturi throat that results in the creation of space/vacuum and ozone gas is drawn into the water or the air which contains ozone is then bubbled up through the water being treated in this process. Ozone has a property that it will react with different metals and such reaction will result in the production of insoluble metal oxides so postfiltration of water is mandatory (Von Gunten, 2003).

The studies of Richardson et al. (2000), Von Gunten (2003), and Xie et al. (2015) described the following advantages and disadvantages for using ozone gas.

1. Ozone is highly reactive and it can show reactions over an extensive pH range. Ozone has powerful germicidal and disinfecting effect than other processes like chlorination and it can be used for treatment against different microorganisms like bacteria, viruses, and protozoa. In a short reaction time, ozone gas can show very effective and strong oxidizing properties.
2. For the treatment of water, ozone gas does not require any kind of chemicals.
3. Ozone gas can be used for the treatment of a wide range of problems like it can be employed for the eradication of different kind of organic, inorganic, and microbiological impurities. Ozone can also be used for the treatment of water taste and odor problems. In addition, ozone can be used for disinfection and sterilization of water to get rid of microbes like viruses, bacteria, and protozoa (such as *Cryptosporidium* and *Giardia*).

4.3.2.2 Disadvantages of the Use of Ozone

1. Use of ozone for water treatment requires specific instruments, which leads to higher equipment and operational costs. Especially skilled professionals, proficient in ozone treatment and system maintenance are also required who are trained in the use of specific instruments and this may be a difficulty to find such trained professional in this process.
2. Ozonation process is a good way for sterilization, but it does not provide any germicidal or disinfection for residual contamination in the process for inhibition or prevention of regrowth.
3. Ozonation process produces by-products which are under evaluation process and it is a possibility that such by-products may possess mutagenic and carcinogenic properties. These by-products may include brominated aldehydes, ketones, and carboxylic acids by-products. This is a good reason to install a postfiltration system in water purification system that may comprise of an activated carbon filter system.
4. Use of ozone gas for water treatment is a system which needs additional reactions such as pretreatment for reduction of water hardness or for the prevention of the carbonate scale formation, the addition of chemicals like polyphosphate is required.
5. Ozonation process requires special mixing techniques because as compared to other gases such as chlorine, ozone is less soluble in water and therefore additional processing is required.

6. Ozone production is a process which requires specific reactions so there are some risks and issues associated with reactions of ozone generation such as fire hazard and toxicity.

4.4 Membrane Technologies

The membrane procedures are in use for the handling of water, these are utilizing separation processes which require pressure and in this method pressure is a force which is very powerful and variable across the membrane for water treatment. These membranes are used for the water treatment and in this process water to be treated is divided into a stream of filtrate and the remaining quantity is called as retentate or concentrate (Peters, 2010). The contaminants present in the feed water could be eliminated using membrane system and are accumulated in the retentate. During this procedure, membranes which are being utilized can be assessed on the basis of pore sizes and the variation in pore size can act as a well-defined barrier (Magara et al., 1998). These membranes allow a constant supply of quality filtered water. In addition to this semipermeability of the membrane, this process ensures a uniform supply of healthy water without microbial contamination (Madaeni, 1999). Purifying units may be comprised of different membranes such as RO, MF, NF, and UF membranes which have properties like high stability during operation, as this procedure is easy to handle if it is designed correctly. Different forms of operations are carried out by using a relevant switch or by executing a command that is already saved in the system. Such operations include start-up, intermittent operation, normal operation, cleaning, flushing, shutdown, or emergency shutdown. These instructions are corrected by the PLC (programmable logic controller) during the operation. The start-up and shutdown do not require any better care and system can itself understand such instructions within few minutes. The design of such systems is modular and it serves as a base for strong flexibility against sudden changes takes place such as a change in the volume of wastewater to be treated and its consequence would be an adjustment in the form of a small amount of carbon footprint for the treatment plant itself. Such treatment plants have many beneficial aspects, for example, cleanliness, density, ease of use, short structure time of these units as well as these units are cost effective and have long-term operational reliability. Some parameters such as membrane intrinsic properties and formation of their new combination with suitable elements and manufacturing design of unit should be followed strictly according to the each specific application's requirement (Alzahrani and Mohammad, 2014). For this purposes, a wide range of filtration membranes available in the market which are designed and used as per their capabilities and requirements and these are discussed further in detail.

4.4.1 Microfiltration

Microfiltration is a process which involves the method of membrane filtration having the same selective types of membrane type. The purpose of microfiltration is sterilization from microorganisms for example, viruses, bacteria, clearance of pigment, and elimination of other impurities in size range of submicron of the particle. The most commonly used commercial membranes that are made up of porous material and have a pore size in the scale of 0.1–1.0 Lm (1 mm = 1000 Lm), with an average pore size of 0.2 Lm. Microfiltration membranes usually require 500 kPa (5 bar) of pressure for its operation (Ang et al., 2015).

4.4.2 Ultrafiltration

Many manufacturing units are taking advantage of UF technology since last two decades (Yamamura et al., 2007). In UF, screening of impurities is carried out on the basis of pore size that lies between 1 and 100 nm depending on the size of impurities. Many suspended, colloidal matter, macromolecules, protozoa, bacteria, and most viruses are separated out using the UF (Nakatsuka et al., 1996). UF membranes can accomplish multiple removal microorganisms, it has a capacity to reduce 7 logs of total coliform bacteria, 4.4–7 log reduction for *Cryptosporidium*, 4.7–7 log reduction for *Giardia lamblia*, and 6 logs or higher for some viruses as MS_2 bacteriophages (Zularisam et al., 2006). This property of UF makes it suitable for the production safe drinking water, without adding the hazardous chemicals or any other thermal treatment (Ang et al., 2015). During the process of UF, two streams are generated one filtrate that is free from contaminants and another retentate that contains all the impurities in the form of physiochemical or microbiological entity. The principal benefit of UF is that it does not require any aided treatment for production of drinking water irrespective of the contaminants present in the feeding water (Yamamura et al., 2007).

4.4.3 Nanofiltration

In the membrane technologies NF is one of the most common technologies that are used for the purification of drinking water. NF works with least consumption of energy per unit filtration of water, a higher rate of reflux and use of exchanged RO membrane system make it possible to achieve a high level of efficiency in this process (Mohammad et al., 2015). The structure of NF membrane lies between the nonporous RO membrane and a porous membrane of UF technology. NF membranes available in the market contain a fixed charge that is used for the separation of surface groups like carboxyl or sulfonic acids.

Hence this technology allows the separation of impurities based on size, electrostatic effect, and ion exchange method. The pore size of NF membrane is about 1 nm so that it can screen out even the small-sized impurities; the electrostatic property of the membrane surface allows only the monovalent ions to pass through it while retaining the most of the multivalent ions. All these advantages of NF make this technology a very helping hand in the selective removal of solute particles (Marchetti et al., 2014). Apart from water purification, many industrial application involves the use of NF technology for the purpose of treatment of pulp during bleaching process, treatment of wastewater from the textile industry, separation of pharmaceuticals from fermentation broths, separation of minerals in the dairy industry, and recovery of metals from wastewater and elimination of viruses (Mohammad et al., 2015). NF is one of the proficient techniques for the remediation of natural organic and inorganic impurities in the surface water. This technique also inhibits the formation of organic materials that are generated as by-products during water treatment by other technologies. In the NF technique, inorganic salts are also efficiently removed due to electrostatic charge of the membrane while macromolecules are separated out on the basis of pore size (Al-Amoudi, 2016).

4.4.3.1 Separation Mechanisms in NF

NF has benefits of lower operational pressure in comparison with RO, and the deposition of organic matter is comparatively low in comparison with UF (Xiong et al., 2014). Separation of molecules which are larger and colloidal in nature can be carried out using sieving mechanism which would be the major filtration method. For the separation of ions and lower molecular weight substances, NF procedure is used as major separation process. Researchers identified the NF rejection mechanisms has following steps (Shirazi et al., 2015):

1. The procedure of wetted surface—Water is polar in nature and it forms a hydrogen bond with the membrane itself and as a result, all molecules which can make linkages as hydrogen bond with the membrane can be sieved and separated.
2. Preferential sorption/capillary rejection—Different kind of membranes can be used these may include membranes which have micropores. In such cases, due to different electrostatic constants of solution and membrane, electrostatic repulsion may occur.
3. Solution-diffusion method—Here in this procedure, the membrane which is used for separation is nonporous and even solute and solvent can be found suspended in the membrane in its active layer and because of the process of diffusion through the active layer of membrane, the solvent transfer may occur.
4. Charged capillary method—In this process, a membrane is used with an electric double layer in the pores, such membrane may

establish rejection. Due to the streaming potential, ions which have the same charge as that of the membrane are attracted by the membrane and counter-ions are repelled by a membrane.

4.4.4 Reverse Osmosis

RO distillation system is recognized as the principal significant and extensively used technology for the formulation of pure water from mineral-rich water. It is estimated that almost half of the installed water purification systems prefer RO technology all over the world, due to its easy adaptability and comparatively low energy expenses and higher efficiencies than concentrations required for other thermal procedures used for water purification (Fritzmann et al., 2007). Furthermore, with the recent advancements in RO-based technologies regarding membrane material and energy expenses, there is a significant decrease in water purification cost thus the market potential for this technology is expanding over the time (Xie et al., 2015).

Global Water Aptitude and International Desalination Association designate the worldwide production of pure water from osmotic water plants are approximately 19.8 billion gallons per day (Malaeb and Ayoub, 2011). Among various other industries, the membrane industry is regarded as a major region in relevance to its worth, which often results in billions. The foremost membrane engineering corporations include Hydranautics (Nitto-Denko), DOW-Filmtec, Toray, CSM, Koch Membrane Systems, and GE Osmonics. Lot of investment incurred by these industries to fulfill customer requirements in relevance to water purification (Shenvi et al., 2015). Furthermore, among various factors, three Ps which are pollution, population, and progress are recognized as major aspects regarding the influence of water purification market. Recently, great attention is given toward advancement and supplication of pure water system due to various complications associated with water pollution, rising human population, and industrial advancement (Werber et al., 2016).

The RO membranes (semipermeable) are recognized as crucial part of ROs, which predominantly permit only specific water molecules passage by inhibiting salt contents under high pressure (Fig. 4.4). The salts and water saturated by using RO membrane can happen only by diffusion mechanism (Shenvi et al., 2015). This is possible when the external pressure is greater than the osmotic pressure ($\Delta p > \Delta \pi$), RO membrane permeability allows the flow of water from concentrated to dilute solutions.

$$J = A(\Delta p - \Delta \pi)$$

where $\Delta \pi$ is the osmotic pressure variation between feed and permeate, Δp is the membrane pressure change, and A is constant that states

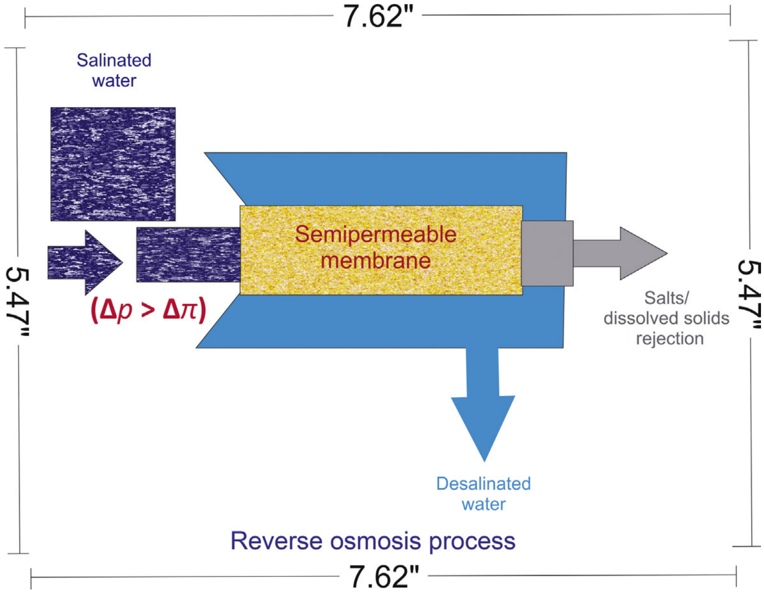

Fig. 4.4 Schematic representation of the process of reverse osmosis.

the physical appearances of various membranes (Post et al., 2007). RO films possess an average pore size of 1 nm and require very higher pressures of almost 80 bars. Also, these high pressures have potential applications in overcoming the osmotic sea water pressure, that is, around 25 bar (Kim et al., 2014). Furthermore, the RO membranes efficiency greatly depends on its water fluxing and salt elimination property. The perfect RO membrane considered to possess salt elimination of almost greater to 99%. Likewise, the NF membranes are employed for water purification applications, although their salt removing efficiency is not considerably higher compared to RO membrane. Most commonly, usage of either NF and RO membrane significantly rely on pure water formulation requirements and applications (Werber et al., 2016).

A classic RO-based system comprises four main procedures: pretreatment, high-pressure forces, salt parting, and posttreatment (Shenvi et al., 2015) and is described in details as follows:

1. *Pretreatment*: Treatment of sea water before its arrival to RO element is recognized to have major importance because polluted sea water is documented to possess a greater quantity of pollutants like colloidal suspension, substantial biological constituents, mud, sand, and numerous embedded solids. Mostly, the osmotic membrane remains more vulnerable for the attack of these polluted constituents, so it is designed in such a way to avoid solid polluted suspensions with effective handling (Pontie and Charcosset, 2015). Moreover membrane blockage by various reasons including fine

particles incorporation, significantly results in irreversible fouling membrane that greatly influences the membranes life, its performance, and formulation cost (Khawaji et al., 2008). Preferably, the various factors tangled in RO pretreatment comprises screening, chlorination, acid treatment, multimedia filtration, microfiltration, and dichlorination (Pontie and Charcosset, 2015). Profound media filters encompass anthracite, sand, and packing layers components ranging from 5 to 10 μm. Microfiltration generally employed for particles retention up to 0.2 μm (Alzahrani and Mohammad, 2014). For pretreatment process of water, various different chemicals are required which includes sodium hypochlorite, ferric chloride as a flocculant, sodium bisulfite to dechlorinate, and sulfuric acid (Malaeb and Ayoub, 2011).

2. *Pressurization*: In this process, untreated water is pumped and for this purpose, high-pressure steel pumps are required. The essential requirements for using pressure depend on the exact type of used water which could be either seawater or brackish water. In this module, the membrane which is incorporated might have the property of tolerating high pressure with sufficient mechanical capability. This kind of operational pumps with high pressure makes the RO system more load (Rezzadori et al., 2017).
3. *Separation*: Membrane is considered as a crucial element of the osmotic system. As the RO membrane performs as a semipermeable barrier that is selectively permeable to water over it and it retains salts. By applying high pressure, most of the salts can enter the permeate side of the membrane (Malaeb and Ayoub, 2011). Moreover, it is possible that a certain volume of dissolved gases is present in the water and at later treatment stages it will be removed. RO membranes which are used commonly utilizes cellulose acetate and diacetates as a basic component but recently, polyamide membranes which are ultrathin in nature are used in the most of the markets (Pontie and Charcosset, 2015). These are available normally in different forms such as hollow fiber or spiral wound design.
4. *The process of posttreatment*: In this phase, infiltrate (permeate) received is exposed to pH alterations ranges from acidic to neutral. Later stages comprise different processes, for example, recarbonation, elimination of carbon dioxide, elimination of H_2S via aeration, and decontamination or disinfection by utilizing calcium hypochlorite or chlorine gas (Li et al., 2013). Demineralization can be done by employing methods like filtration or chemical injection (Lin et al., 2014). These sections are generally essential to get better water taste and also fulfill the last essentialities of the treated water. Management of brine and various other chemical compounds produced during pure water formulation is crucial before its expulsion in seawater (Li et al., 2013).

4.4.4.1 Difficulties Associated With Process of RO

Scaling

Membrane filtration of seawater has enhanced the absorption of numerous soluble salts but when solubility such salts extends to supersaturation point, they decline for further precipitation and form outer membrane scales which in turn results in lowering RO system efficiency (Shmulevsky et al., 2017). The use of antiscaling agents is the extensively implemented method to avoid scaling of different salts such as silica, iron, barium sulfate, calcium carbonate, gypsum, etc. The incidence of such salts in various amounts highly depends on feeding water (Pramanik et al., 2017). In the start of this process, on the outer surface of membrane antiscaling compounds are accumulated to avoid the initiation of scale development. Most frequently used such antiscaling compounds include surface active reagents, organic phosphates and phosphonates, and organic natural polymers that significantly obstruct, formulation, development, and kinetics of crystal nucleation (Dahdal et al., 2014). Likewise, various scales formation by silica enhances major complication during water purification process as it requires great expenses to overcome these situations. Also, the incorporation of antiscaling substances may not significantly reduce silica because of various factors impact on silica precipitation. Carbonated scales could avoid by regulating the pH of water ranges at 4 and 6. Various studies documented the enhancing levels of bicarbonate for significant reduction of gypsum scales in internal water feeds (Kempter et al., 2013). The bicarbonate adsorption of crystal surface results in reduction of gypsum scales on surface membranes. Superficial coating of polyacrylamide material results in accumulation of scales on the membrane surface, where gypsum is used for reduction of the scaling inclination (Radu et al., 2015). Feed can be pretreated by different methods like pH modification, NF/UF, and ion exchange may also assist in the reduction of scaling (Zhao et al., 2014). Another method which is known as flow-reversal mechanism can also be used to prevent the process of scaling has also been reported. It is possible that flow can be reversed before the start time of the process with the help of replacing the supersaturated brine solution with the unsaturated raw water and this makes the nucleation time as zero thus determining the beginning time (Kazner et al., 2014).

Boron Removal Process

The removal of boron can be done by various membranes; this is considered as modern topic of interest that remains a task today. Regarding, the various WHO regulations, the permitted quantity of boron in pure water should not be more than 0.5 mg/L (Park et al., 2016). The efficacy of RO progression for boron exclusion has not more enough, preferably due to the presence of various elements in water. For instance, boron is present in the form of uncharged boric acid in the seawater at normal pH and this can pass through semipermeable membrane easily like water with a rejection value of <80% (Cengeloglu et al., 2008). Borate ions come into being at high pH, which displays almost 99% rejecting level (Dydo et al., 2014). Therefore, such properties like pH of the respective solutions and ionic strength can display crucial role in leading the boron rejection during desalination. Moreover, for effective boron exclusion, RO plant possesses two or more phases. At the first phase, irrespective of pH modification, contaminated water is fed to the RO membrane at a very high pressure and at this level; most of the dissolved contaminants are eliminated. At later phase, the water containing remaining impurities is incorporated with high pH at low-pressure RO membrane for removal of boron (Park et al., 2016). Alternative method employed for boron eradication involves, first pass the boron-contaminated water through RO membrane having high pressure and then this water is passed through the selective medium containing ion-exchange resin for removal of boron that is, boron selective resin (BSR). BSR method have appreciable results for the elimination of boron but this great technology requires high initial and operating cost that is considered to be the major disadvantage in the removal of boron from contaminated water, so further research and studies are suggested for the identification of cheap and economical alternatives for the removal of boron (Shenvi et al., 2015).

Brine Disposal

The rejected water containing high amounts of salts and minerals that are removed during the purification of contaminated water by RO membranes is known as brine. Along with dissolved minerals and salts brine water also contains many organic compounds, particulates of antiflocculants, antiscalants, acids, metals, and metalloids (Chaea et al., 2017). The most in use brine elimination practices include direct release into sea, release on substantial surface, and flushing into the open drains or sanitary channels. Such disposal of highly salinized water at sea or inland surface channels brings lot of environmental and ecological threats. Nonstop flow in sea has a significant effect on the algal compounds and plant life and outcomes in mud development. Exclusion of brine into the pond is mostly approved for local RO desalination plants that serve in the arid and semiarid regions where the sea is not available for direct discharge, in the pond disposal the brine water is evaporated by the abundance of sunshine and minerals are collected at the base of the pond (Ng et al., 2008). Though, vanishing ponds devour too much space, high salinity discharge may disturb the soil and plants efficiency.

Disbanding the brine along with seawaters, assisted in plummeting the ecological influence by dilution. The diffusion of brine into the sea is affected by the depth and velocity of discharge (Chaea et al., 2017). SAL-PROC technology is used that is demonstrated as a combined protocol for removal of soluble constituents from inorganic saline water in a sequence, by various evaporation and cooling technique along with mineral separation (Shenvi et al., 2015).

The components extracted by various procedures include sodium chloride, gypsum, calcium carbonate, calcium chloride, and magnesium hydroxide are of great quality and adopted by numerous water companies. Elimination of scale components of feed water resulted in a smaller amount of brine and advanced recovery rates (Chaea et al., 2017). It is claimed that a two-stage brine alteration seawater RO purification system (brine alteration system, BAS) is in the capacity to produce the potable water having total dissolved solids less than 200 ppm (Mohamed et al., 2005). This technology reduces the manufacturing cost by 20%–25%. Further, the studies also state that the brine produced in RO plant is processed by the electrodialysis (ED) which reduces the absorption of salts in the feed and it increases the value of RO permeate (Ng et al., 2008).

4.4.5 Future Development of Membrane Technology

Currently, significant expansions occurred in manufacturing membrane by focusing attention on the combination of different membrane procedures in thermal parting techniques and chemical or biological alterations (Cohen-Tanugi and Grossman, 2012). By keeping these, products worth, highly compacted creation units and methods with better efficiency, sustainable, low energy consuming, and the ecologically responsive process can be attained (Zhao et al., 2012). The future expansion of membrane skill will be inclined to various aspects such as:

- The extent of sanitization of the fluid to be preserved as expected from the customer or enforced by laws, driven by various forces for solutions development. For this reason, these would be primary environmental features such as enhancing pollution, stricter discharge regulations, and escaping of chemicals (Kang and Cao, 2014).
- A decrease in treatment costs for increasing operational experience and longer life of the membrane system (Ghaffour et al., 2013).
- The numerous membranes formulation altered to definite applications (Cath et al., 2006).
- Improved struggles for reducing membrane fouling (Mansouri et al., 2010).

- Reliable procedure monitoring (Cath et al., 2006).
- Consistent expulsion control (Cath et al., 2006).
- Standard plant perceptions with a feasible version of each individual situation in place (Ghaffour et al., 2013).
- Recognition of plug and play concepts (Cath et al., 2006).
- Extensive use of different methods which include agreements on Make and Self-Operate or Make Operate-Transfer, and based on quality necessities, membrane technology combination of water management system.

4.4.5.1 Electrodialysis

This technology signifies a modern liberal electromembrane partitioning method. Particularly, for the brackish water purification demonstrating the foremost demand for skill, ED is currently recognized to be in great competition with the normal RO (Tsiakis and Papageorgiou, 2005). There is a growing trend to use ED for the wastewater reclamation and purification of water effluents in the pharmaceutics and food industries. The main advantage for using this technology is the electromembrane departure process that does not compromise on health and nourishing attributes of the ending products for example, by addition of coagulants or restoring constituents (Bernardes, 2016). ED process (Fig. 4.5) includes water passage amid two electrodes with opposite electrical charges. The negative electrode attracts the various metal ions that present in contaminated water while the positive electrode attracts nonmetal ions. Both metal and nonmetal ions can be removed from the electrodes (Chen et al., 2016).

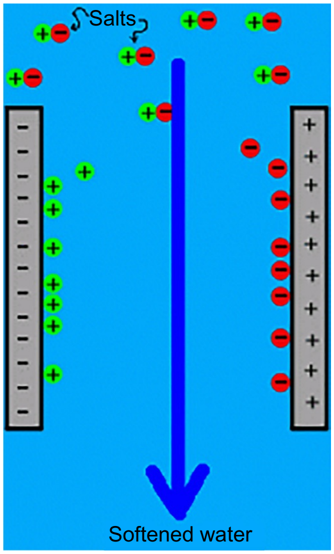

Fig. 4.5 Process of electrodialysis.

ED water treatment is generally used for hard water, which possesses 500 mg/L calcium carbonate. Recently, some latest components were added in ED process that results in improved proficiency of ED with great control of polarity. This technique is regarded electrodialysis reversal (EDR) and it has the capacity to reduce the scaling and fouling problems which are very common in ED process (Lee et al., 2013).

4.5 Advanced Oxidation Process

Some researchers describe the advanced oxidation process (AOPs) to define a procedure of hydroxyl radicals (OH) for organic and inorganic oxidation of water layers (Ganiyu et al., 2015). There are many AOPs process used around the world. But, two main AOPs are described in this chapter that includes ozone along with H_2O_2 addition and UV radiation along with H_2O_2 accumulation. AOPs may have numerous advantages in water management technology, for instance, oxidation of artificial organic chemicals, taste, color, and odor inducing agents, sulfide, various minerals (Fe, Mn) and demolition of DBP precursors before chlorine addition (Sirés et al., 2014).

4.5.1 Ozone With H_2O_2 Addition

The addition of H_2O_2 with ozonated water is simple technique having a powerful reaction of H_2O_2 with molecular ozone, which enhances the formulation rate of OH. Due to this reason, an ozone-H_2O_2 purification system is greatly used to improve the absorption of hydroxide radicals that have a strong oxidizing potential compared to molecular ozone, and so quickly results in molecular ozone reduction. That is why H_2O_2 is highly recognized for its usage in the process of ozonation rather than disinfection (Hey et al., 2014). The added ozone-H_2O_2 method is used for the extinction of off odors, color elimination, and micropollutants damage, such as volatile biological mixtures, pesticides, and herbicides (Wang et al., 2014). Stoichiometric investigation proposes that optimal H_2O_2 to ozone ratio is around 0.3:1 (mg/mg). Nevertheless, detailed studies have proposed that best ratio is greater in the range of 0.5:1–0.6:1 mg/mg (Afzal et al., 2015). The typical mechanism in which ozone is added with H_2O_2 involves incorporation of influents water as a constituent of the system and ozone as intense gas, which is bubbled finely from the bottom of the water tank by diffusing technology (Hey et al., 2014). The complicated reaction chemistry involved among ozone, H_2O_2, normal biological constituents, and added ingredients from water, it is not clearly evident that either such traditional structure is considered to be the best design for an ozone-H_2O_2 management method. By various future research studies and recent advances in engineering design technology, its efficiency could be significantly improved by the reduced level of ozone and H_2O_2.

4.5.2 UV Irradiation With H_2O_2 Addition

UV irradiation in the presence of H_2O_2 deteriorates the constitute OH. Adding H_2O_2 to UV irradiation influents is recently employed for the demolition of groundwater micropollutants, but at the same time, it possibly serves as a basic component for reactions as in other AOPs, thus ensures better taste, odor, and the color of the water. Various reactions among UV and H_2O_2 for the formation of OH operate at much slower rate than the reactions carried out between ozone and H_2O_2 (Fujioka et al., 2017). Although in numerous water purification strategies, UV irradiation is considered to be the better option than ozone generation system due to the complexity of the process and feeding system. Conversely, a high concentration of H_2O_2 (5–20 mg/L H_2O_2) residues are required due to slow OH manufacturing reactions in UV-H_2O_2 systems (Oh et al., 2014). Consequently, the implication of this method in drinking water purification, both by the process modification to use less H_2O_2 and a management method should be connected to reduce the H_2O_2 components to required levels (<0.5 mg/L) prior to water incorporation in supply system (Fujioka et al., 2017). The numerous possibilities offered for reducing the H_2O_2 residuals comprises of using thiosulfate, chlorine, granular-activated carbon, or sulfites (Fatta-Kassinos et al., 2011).

4.6 Ion-Exchange Technology

Ion exchange, which is abbreviated as IX technology, is being employed in various biochemical and ecological manufacturing areas for extended periods. But, nowadays its use in water softening is very common, which involves the removal of Mg^{2+} and Ca^{2+} ions from hard water, either at water purification plant or by implying proper time for using a treatment procedure and also for industrial applications, for example, the formulation of pure demineralized water (Atalay and Ersöz, 2016). Although, with various limitations being related to numerous inorganic compounds, ion-exchange treatment gains considerable interest for water improvements system. Some of the most important components or pollutants removed with ion-exchange technology are arsenic, nitrate, barium, selenium, radium, lead, chromate, and fluoride. Early studies carried out in the 1980s proved that almost 400 societies have considerably greatest amount of nitrate up to maximum concentration level of 10 mg/L as nitrogen and 400 societies near the sea have an excess of fluoride content that is maximum concentration level of 4 mg/L (Jacob, 2007). Recently, new contaminants detected in groundwater are perchlorate ($C1O_4^-$) ions that are a significant constituent of rocket fuels. The California Department of Health Services has accepted a perchlorate action near of 18 g/L, and considered exchange technology as a perfect system for the perchlorate ion exclusion from polluted water (Fox et al., 2014).

While using ion-exchange technology, the knowledge-based process is usually planned as a fixed-bed procedure for packing of synthetic resins. Therefore, during water passage through the resin bed, potential contaminants existing in water are replaced with resin ions on surfaces, thus eliminating the contaminant ions from the water by directing them on the resin. The resin is normally redeveloped to eradicate the contaminant from the resin surface and replace it with different interchangeable ions (Mazur et al., 2016). There are four main categories of ion exchange resins: strong acid cationic (SAC) resin, weak acid cationic (WAC) resin, strong base anionic (SBA) resin, and weak base anionic (WBA) resin (Nikoloski et al., 2015). The details for these resins are presented in Table 4.2 that presents different ions which can be screened out with the help of different resin type, the resin renewal requirements. The terminologies used in the table designate as SAC and WAC resins are employed for the removal of positive ions from contaminated water (e.g., Ra^{2+}, Ba^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}), whereas SBA and WBA resins are formulated for the removal of negative ions (anions) from contaminated water (e.g., ClO_4^-,NO_3^-,$HASO_4^{2-}$,SeO_3^{2-},SO_4^{2-}, etc.).

SAC resins mostly activate over a widespread pH values ranges 1–14, while WAC resins can merely function at pH >7. During water softening applications, SAC resins may eradicate together carbonated and noncarbonated firmness, while WAC resins can first eliminate carbonate hardness. In addition, WAC resins are preferred over SAC because of their easy regeneration, and not resulted in sodium enhancement compared to SAC (Fries et al., 2017). Furthermore, the additional cost of ion-exchange technology is less as compared to added inorganic exclusion procedures, for example, lime softening techniques, high pH ppt, and high-pressure membranes (RO membranes). For instance, the total rates of ion-exchange technology for the exclusion of nitrate ions from groundwater is valued to 0.4 t–0.5$/gpd (Bergquist et al., 2016). However, commercial applications of ion-exchange technology at large scale are challenging because of the high level of waste production from purification process. Although, the volume of waste produced by this process is not so large and can only account 2%–5% of the total treated water yet the waste produced, encompasses a high level of acid (HCl), base (NaOH), or salt (NaCl). In addition, the waste stream may also hold higher levels of pollutants (e.g., NO_3^-,$HASO_4^{2-}$,Pb_2^+, etc.) that should be treated before the wastewater is disposed of in sea (Alzahrani and Mohammad, 2014). Therefore, the removal of waste components from water is considered as a principal application of ion-exchange technique at commercialized water purification plants whereas treatment systems present in areas which are near to sea and ponds may have the choice of waste disposal into nearby oceans. Conversely, for the inland plants there exists no cost-effective procedure for the removal of the waste stream (Manos and Kanatzidis, 2012).

4.7 Biological Filtration

Various techniques as mentioned above are based on many physiochemical working principles. However, the water purification industries not only influenced by physical and chemical procedures to properly achieve the water purification and quality standards. Advancement in various biochemical methods in water purification is reported and now being adopted in water treatment plants. This technology is gaining popularity due to increased incidences of infectious out breaks and safety concerns about the existence of microorganisms in water (Kvartenko et al., 2016). Among these biological processes, biological filtration is recognized as foremost an important operative method to produce pure water free from biological contaminations. This was especially compelled by concerning the enhancement of biodegradable organic matter (BOM) absorption, because of natural water ozonation. Moreover, there is great concern regarding increased BOM levels that may results in higher organic contaminants recreation in the circulation arrangements. Therefore, by the implementation of biological filtration technique, various water treatment plants result in a reduction of BOM absorptions in the pure water, which is already present into the circulations plant (Xie et al., 2015).

The overall development in the design of organic filtrates is to encompass a thin sand layer (6–12 in) below the granular activated carbon (GAC) or anthracite media (Sierra et al., 2017). Sometimes this layer of sand confronted with major problems during the filtration process. Biological filters also have some problems in the filtration so we can overcome this problem with the help of dual filtration method, by ensuring the exclusion of chlorine or chloramine that they should not present in the final pure treated water. But, there are many queries which need more advanced research and study to improve the process of biofilters. Furthermore, various water purification systems had recognized the importance of incorporation of chlorine (4–5 mg/L) to contaminated water during washing. This addition of chlorine significantly improves the biological resistance of filtrates, inhibits the multicellular organism initiation and progression in filters, and filters routes length enhancement by lowering frequency of headless buildups. However, more advanced research studies are required for addressing various problems regarding biofiltration functionality. Biofilters are also in use for the treatment of drinking water to reduce these contam-

Table 4.2 Types and Characteristics of Ion Exchange Resins

Resin Type	Functional Group	Ions Removed	Regeneration	Reference
Strong acid cationic (SAC) resin	Sulfonate RSO_3^-	Total hardness, Mg^{2+}, Ra^{2+}, Ba^{2+}, Pb^{2+}, etc.	Regenerated with HCl or NaCl	Millar et al. (2015)
Weak acid cationic (WAC) resin	Carboxylate $RCOO^-$	Carbonate hardness, Mg^{2+}, Ra^{2+}, Ba^{2+}, Pb^{2+}, etc.	Regenerated with HCl	Al-Samadi (2014)
Strong base anionic (SBA) resin	Quaternary amine $RN(CH_3)_3^+$	$NO_3^-, SO_4^{2-}, ClO_4^-, HAsO_4^{2-}, SeO_3^{2-}$, etc.	Regenerated with NaOH or NaCl	Bazri et al. (2016)
Weak base anionic (WBA) resin	Tertiary amine $RN(CH_3)_2H^+$	$ClO_4^-, HAsO_4^{2-}, SeO_3^{2-}, NO_3^-, SO_4^{2}$, etc.	Regenerated with NaOH, or $Ca(OH)_2$	Fries et al. (2017)

inants. Biofilters also reduce the many inorganic contaminants such as bromate, perchlorate, chlorate, nitrate, and selenite (Mimura et al., 2017). But the use of this method still needs many types of research for using this method at the large scale.

4.8 Biosorption

This method can remove the toxic substances from the water by using the physiochemical pathways (Kabir and Chowdhury, 2017). This is the relatively new method which is more extensively used for exclusion of heavy metals from contaminated water. Biosorption is obtained from the nonliving biomass such as lignin bark, shrimp wastes, algal, and microbial mass, for example, bacteria, fungi, and yeasts. Algae have evidenced to be potential heavy metal biosorbents (He and Chen, 2014). The significant advantages of biosorption compared to prevalent treatment methods have reasonable cost, high efficiency, no further nutrients necessities, biosorbents recreation, reduction of biochemical by-products, and enough metals reduction probability (Ngo et al., 2015). However, the disadvantages of biosorption are initial saturation, less chance of biological development since the cells are not significantly metabolized and numerous complexities regarding alteration of metals valency (Gaur et al., 2014).

Normal materials like chitosan, clay, zeolites, and certain waste goods are known as fewer rate adsorbents. Chitosan has recognized as an important metal binder and has a very low-cost stimulated carbon (Wang and Chen, 2014). Activated carbon is the most widely used adsorbent in the world but it is a very affluent material so it cannot be used on large scale due to cost inefficiency. Shrimp, lobster, and crab shells are used to produce chitosan in countries which have a huge marine product such as Japan. These wastes can be got from fishery industries at very low cost (Anastopoulos et al., 2017). Clay is a good substitute for activated carbon. It is a significant inorganic constituent in the soil. Clay also have the higher surface area, thus providing more adsorbent surface to bind with impurities in water, this makes it potential biosorbent for water treatment plants. However, the negative charges on clay minerals are responsible for attracting positive toxic heavy metal ions (Liu et al., 2014). Zeolites have better ion exchangeability. Massive sediments of zeolites in various regions include Mexico Iran, Jordan, and Italy that offer decent possibilities for the removal of heavy metallic ions from wastewater at less cost (Dinu and Dragan, 2014).

4.8.1 Biosorption Mechanism

The biosorption method includes two phases as subsequent liquid phase (solvent) and solid phase (biosorbent), which has a capacity to absorb specific substances from the relative classes to be sorbed (metal ions). Moreover, there are numerous methods for metal uptake by different cells because of complex microorganism's structure. Therefore, the biosorption mechanism is the very complex procedure. Regarding the cell metabolism, biosorption can be categorized into two types that are metabolism dependent and nonmetabolism dependent. This process has three subclasses based on the metal removal site in solution, for example, intracellular accumulation, extracellular accumulation, and cell surface precipitation (Li et al., 2015). Intracellular accumulation is the outcome of transverse metal transportation by the cell membrane that greatly associated with cell metabolism. Besides, this situation reveals that such sort of biosorption could happen only with feasible cells. Indeed, the biosorption, in this case, is not considered to be much faster because of more time required for relative microbial reactions. The various connections between the heavy metal and cells functional groups significantly result in a cell surface sorption based on physical adsorption, ion exchange, and complexation, which is independent to the metabolism (Ramrakhiani et al., 2016). Cell walls of microbial by-products are most commonly composed of various polysaccharides, proteins, and lipids, which have several metal binders functional groups exemplified as carboxyl, sulfate, phosphate, and amino groups. Nonmetabolic biosorption is comparatively quick and could be effectively reversed (Wang and Chen, 2014). During precipitation, the heavy metals absorption can occur both in solution and on the cell surface (Ramrakhiani et al., 2016). In these processes, the precipitation may not eventually recognize to be cell reliant, if it occurs after metal and cell interactions.

4.8.2 Transport Across Cell Membrane

Transport between cell membrane is associated with cell metabolism. Biosorbent examination of higher metal absorptions was not carried out due to the toxicity of some elements. Indeed, there is less evidential research data regarding this type of adsorption process. Moreover, transportation of heavy metals could be facilitated by the identical procedure used to supply metabolically momentous ions, for example, K^+, Mg^{2+}, and Na^+. There is also confusion regarding the existence of heavy metal ions having identical charges and ionic radius of critical ions (Ramrakhiani et al., 2016). Furthermore, it is not connected with metabolic activity. Biosorption by biotic microorganisms fundamentally consists of two stages. First, independent metabolic binding that the metals are bound to anywhere in relevant cells and second, dependent metabolic intracellular uptake, where the metal ions are replaced by the cell membrane into the cell (Pokethitiyook and Poolpak, 2016).

4.8.3 Physical Adsorption

Physical adsorption can occur by Van der Waals interactions, radionuclides which predominantly prevail in aquatic environments like sea are grouped by water microbes (Thommes and Cychosz, 2014). A study about this mechanism demonstrates that uranium and thorium biosorption by various fungal strains of *Rhizopus arrhizus* found by physical adsorption in chitin cell-wall arrangement (Fomina and Gadd, 2014). Electrostatic interfaces are accountable to copper biosorption by bacterial spp. *Zoogloea ramigera* and algal *Chlorella vulgaris*. While, physical adsorption is accountable for zinc, cadmium, copper, nickel, and lead biosorption by *Rhizopus arrhizus* (Fomina and Gadd, 2014).

4.8.4 Ion Exchange

Ion exchange methods have extensively been used to eliminate heavy metal ions from waste polluted water regarding their elimination, effectiveness, and effectual kinetics. Conversely, several researchers have proposed that ion exchange is not the only single effective method used for metal biosorption (Fomina and Gadd, 2014). The existence of low-molecular-weight ions in cell walls and membranes such as Na^{+1}, Ca^{2+}, K^{+1}, and Mg^{2+} could be replaced by metal cations such as Cu^{2+}, Cd^{2+}, Co^{2+}, and Zn^{2+}, subsequently result in bio sorptive absorption of metals. The gram-positive bacteria, from largely the genus and from members of *Bacillus* genre, had improved capacity for metal binding due to its substantial negative charge density (Gupta et al., 2015).

4.8.5 Complexation

The biosorption of heavy metal ions from respective solutions might arise through the composite development on the cell surface after various interrelations among heavy metal ions and activated binding places. Metallic ions could be fixed to the single related ligand through chelation (metal ion formulation by ring structure). Besides complexation might occur by either covalent or electrostatic interaction (Fomina and Gadd, 2014).

4.8.6 Precipitation

The precipitation mechanism in several cases describes the development of insoluble inorganic metal precipitates; sometimes precipitates may also be formed in organic metal biosorption process. Precipitation may sometime show its dependence on cellular metabolism (Pokethitiyook and Poolpak, 2016). In case of metal biosorption metabolism, it is frequently linked with an effective defensive microbial system. These mostly show quick reactions in the presence of toxic metallic ions, significantly result in compounds formulation that supports the precipitation progression. Whereas, in case of metabolic independent mechanism, it might result in chemical relations between the metal and cell surfaces (Hansda and Kumar, 2016).

4.8.7 Factors Influencing Biosorption

Literatures showed that there are four important factors affecting biosorption. These are temperature, solution pH, biomass concentration, and occurrence of other metal ions.

Temperature: Temperature in the range of 20–35°C does not seem to affect the biosorption efficiency (Ramrakhiani et al., 2016).

Solution pH: The pH is the most vital factor in the biosorption process due to its effect on the functional group's activity of biomass, the solution chemistry and competitive metallic ions and heavy metals interactions (Ramrakhiani et al., 2016).

Biomass concentration: Biomass concentration in related formulations seems to be more effective on the particular uptake. Specific uptake rises as biomass concentration is reduced (Ramrakhiani et al., 2016).

Presence of other metal ions: In various cases, biosorption is discerning. Biosorption is commonly used for reducing the definite quantity of heavy metal in wastewater and elimination of this specific heavy metal may affect existence of other heavy metals. Thorium adsorption by *Rhizopus arrhizus* is unchanged due to the existence of further ions like Fe^{2+} and Zn^{2+} in solution whereas Uranium adsorption with *Rhizopus arrhizus* is affected by the occurrence of Fe^{2+} and Zn^{2+} (Gupta et al., 2015).

4.8.8 Comparison Between Low-Cost Adsorbents and Active Carbon

4.8.8.1 Chitosan

Chitin is a structural polysaccharide of crustaceans, insects, and some fungi and produced by numerous living organisms. Thus, it is considered to be second most commonly occurred biopolymer after cellulose (Boddu et al., 2003). Fungal cell walls comprise chitin and chitosan, which have been verified through researchers to sequest metal ions. It was claimed that *Rhodotorula* sp., which is a type of fungus, contained chitin as a cell-wall polysaccharide (Franco et al., 2004). Chitosan, which had a similarity in molecular structure to cellulose, is formed by alkaline N-deacetylation of chitin. Chitosan is a low-cost material with resulting characteristics: nontoxic, fine mechanical power, hydrophilic nature, good bonding properties, etc. Thus, chitosan is used as a chelating polymer for metals elimination (Franco et al., 2004). Contrary to natural chitosan, synthetic polymers have high reactivity and process capability due to it fixed molecular structure and polycationic nature (Wang and Chen, 2014). The occurrence of various amino and hydroxyl groups in chitosan may substantially play a role as active sites; this makes chitosan a beneficial adsorbent to eradicate heavy metals ions and coloring compounds (Boddu et al., 2003). Chitosan constituents recognized to have a good adsorption capability that resists acidic environment (Wang and Chen, 2014). Chitosan found to be very responsive to changing pH because it forms gels with different characteristics depending on pH values of solution (Mcafee et al., 2001). Cross-linking reagents such as glutar aldehyde, glyoxal, formaldehyde, epichlorohydrin, ethylene glycon diglycidyl ether, and isocyanates have extensively been used in order to enhance chitosan's efficiency to remove impurities from water (Saifuddin and Kumaran, 2005).

4.8.8.2 Zeolites

Zeolites are recognized as most commonly occurring hydrated alumina silicate minerals with a cage-like structure and these from the class of tectosilicates. Its structure consists of 3-dimensional framework of SiO^{4+} and AlO^{4+} tetrahedral (Lameiras et al., 2008). Moreover, various zeolitic compounds are formulated by modification of glass-rich volcanic rocks (tuff) along with fresh water in different lakes or by seawater (Blanchard et al., 1984). There is Al^{3+} ion surrounded by the tetrahedron structure of four oxygen atoms and a negative charge is produced in the lattice by the isomorphus replacement of Si^{4+} by Al^{3+}. The total negative charge is well adjusted by replaceable cations, which in numerous formulations containing Pb, Zn, Mg, and Cd are exchangeable with positive cations (Lameiras et al., 2008). These ions (Na^{+1}, Ca^{2+}, and K^{+1}) are relatively nontoxic which makes them especially convenient to remove toxic heavy metals. Zeolites are specially used in order to remove and purify cesium and strontium radioisotopes (Chojnacki et al., 2004). Clinoptiolite is the most abundant mineral among the different known type of zeolites which belongs to the HEU-type zeolite group. Many researchers investigated the ion-exchange capacity of clinoptilolite. It was observed that clinoptilolite obtained from diverse areas exhibit changed behaviors in ion-exchanging process (Baskan and Pala, 2014).

4.8.8.3 Clay

Clays are hydrous aluminosilicates and broadly defined as those minerals that make up the colloid fraction ($<2\,\mu m$) of soil, sediments, rocks, and water (Álvarez-Martín et al., 2016). Usually, clay is known as the materials that become plastic when mixed with small amount of water. There are three basic types of clays: aremicas (such as montmorillonite), smectite, and kaolinite (such as illite). Clays always exhibit transferable cations and anions on its external area. Clay may uptake heavy metal cations because of its total negative charges on its surface, thus positively charged cations can neutralize the negative charge. The greater surface area of clays (up to 800 m^2/g) may result in high adsorption capability (Olu-Owolabi et al., 2016). Montmorillonite clays have smallest crystalline compounds, biggest surface area, and maximum cation exchange capacity (CEC). Therefore, montmorillonite clays have the high sorptive capacity. For example, exclusion of mercury by montmorillonite was five times larger than possess by kaoline. Moreover, clays can be altered to expand its adsorption capability (Belhaine et al., 2016). There are two prevalent methods for clay modification: intercalation and pillaring and acid activation.

4.8.8.4 Activated Carbon

Activated carbon is produced from environmental wastes with high carbon content. Lignocellulosic and coal materials have been used as raw materials planned for manufacturing of activated carbons. There are two approaches for preparing activated carbon that can be used in water purification processes: physical activation and chemical activation. Activated carbon has good potential for adsorbing heavy metals because of its greater surface area, microporous ability, and chemical complexity of its external area. There are two forms of stimulated active carbon: H-type and L-type (Zelmanov and Semiat, 2014). The H-type carbon adopts positive charges, when introduced into water or treated with strong acids and is characterized as hydrophobic in nature. The L-type carbon is a stronger solid acid than the H-type carbon which assumes a negative charge in water which neutralizes strong bases and is hydrophilic. Activated carbon is categorized into four basic classes based on its physical appearance. Powders (PAC), granular (GAC), fibrous (ACF), and clothe (ACC). Nowadays, commercialized activated carbon (CAC) has more extensively used worldwide (Mudakavi and Puttanna, 2016).

4.9 Conclusion

Great advancements observed in purification processes of water in recent years. Various water treatment industries have been adopting modern technologies but at a slow incremental pace. From the last 20 years, there has been increasing development in the occurrence of new technologies that remaining to be introduced, established, and demonstrated, into the municipal water purification. Most of these modern technologies comprise of UV irradiation, membrane filtration, advanced oxidation, ion exchange, and biological filtration. Advancement of water purification industry is not limited to these technologies. Although these technologies have potential market value due to their applicability and reliability to large-scale municipal water treatment plants, for example, costs of these treatments continually are going down that result in increasing applications at the industrial level. Today due to technological advancement, each and every physiochemical and biological impurities from water can be excluded during water treatment, but application mainly depends on the cost of the process. With growing population across this globe, more resources are required to invest in water purification research to provide safe, clean, and wholesome water to every person on this globe.

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5

MULTIELEMENT AND ISOTOPIC CHARACTERIZATION OF BOTTLED MINERAL WATERS ON THE ROMANIAN MARKET

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5.1 Introduction

Water is one of the most essential components of life, it contributes significantly to health, and good health is the essence of development (Quattrini et al., 2016). Safe and good quality drinking water is the basis for good human health (Yabanli, 2012) and pollutants with potentially harmful effect, like heavy metals, or pesticides, fertilizers, may deteriorate the quality of drinking waters (Krachler and Shotyk, 2009).

Natural mineral water means "microbiologically wholesome water, within the meaning of Article 5 of Council Directive 80/777/EEC, originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bore exits," as it is stipulated in European Regulation (S.I. No. 282/2016—European Union). Purity at source and their constant level of minerals are special characteristics that might be distinguished as natural mineral water from ordinary drinking water. Spring water is destined for consumption in their natural state, which is maintained by bottling at the source.

According to the Food and Drug Administration (FDA, 2002), mineral water arises from a geologically and physically protected underground source, characterized by constant levels and relative proportions of minerals and trace elements at the source. Spring waters are natural outflows of groundwater to the surface area (Jasik et al., 2017). The origin of geologic landscape through the groundwater passed influences the composition and properties of natural mineral and spring waters (Garboś and Święcicka, 2013).

In Romania, mineral water consumption is recognized over time. As a result of its complex geological structure, Romania has a large variety

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of mineral water types, amounting to 2000 springs over the entire territory (Feru, 2004). Among them, an outstanding position is occupied by the naturally carbonated mineral waters, whose origin is associated with the postvolcanic phenomena of the Neogene volcanic domain of the Carpathian Mountains, which displays the most extended surrounding of volcanic gas outflows in the entire Europe. In terms of their geologic setting, most of the mineral water accumulations occur in carbonated rocks that include limestones, calcarenites, and conglomerates (about 45%), next in pyroclastic and andesite (about 25%), in detritic deposits consisting of sand and gravel (about 25%), and to a limited extend in sandstones and crystalline schists (Feru, 2004).

The therapeutic use of the mineral water in Romania dates back to the Roman period, while the tradition of bottling natural and curative mineral waters is over 200 years old. However, it does not mean that all waters that are sold in the Romanian market are 100% healthy. Consumers should take into consideration several important factors when they buy a mineral water, such as calcium, sodium, and magnesium concentration. Still or sparkling mineral waters that have a high amount of calcium (above 100 mg L^{-1}) are not recommended for people who have kidney or bile problems. Hypertensive persons and those with cardiovascular disease should be very careful about sodium intake. Medical advice suggests to drink mineral water with a sodium content less than 20 mg L^{-1}. Studies show that a still or sparkling water with a high concentration of magnesium is healthy for the metabolic system. The maximum magnesium content that an adult should consume daily is about 400 mg L^{-1}.

The bottled water sector has promoted its product based on purity and health considerations (Platikanova et al., 2017). Increased consumption of bottled mineral waters in recent decades implies a greater need for quality monitoring (Dos Santos et al., 2016). The origin of bottled waters can be quite diverse and includes aquifers, springs, reservoirs, or even tap water (Astel et al., 2014).

It is well established that the chemical composition of natural waters is controlled by many factors that include chemistry of atmospheric precipitation, mineralogy of the rocks encountered along the flow path, residence time of the groundwater in the aquifer, climate, and topography (Güler et al., 2002). Also, the pollution of waters, as a consequence of anthropogenic factor, can influence the water quality. Therefore, each bottled water brand has its own characteristic chemical properties that are defined by a unique combination of these factors. Several studies have shown that high levels of minerals are not well liked (Platikanov et al., 2013). Bottled water is considered as an important element in the human diet and plays a major role in the intake of a number of nutritional and potentially toxic elements. There were situations when bottled waters represented cases of fraud and denaturation of the product (Spangenberg and Vennemann, 2008). In the literature are presented only a few studies about the long-term health effects of these types of water on human and animal (Qiu et al., 2015). High-quality drinking water is a fundamental element of good public health. The consumers should be informed of the mineral composition of drinking waters; these may be a source of some elements like calcium and magnesium in the diet and could be important for those who are marginal for these minerals intake.

In the EU countries, there are over 1230 recognized brands (European Union, 2005). In many countries, there are regulations specifically governing the sale of bottled mineral water. In the European Community (European Union Directive 2003/40/EC, 2003; European Union Directive 1996/70/EC, 1996; European Union Directive 1980/777/EEC, 1980), one states that bottled water must be definitely groundwater, and clearly distinguishable from ordinary drinking water by its nature. The EU had passed regulations for action levels for trace elements in drinking and bottled water (European Union Directive 2003/40/EC, 2003; European Union Directive 1998/83/EC, 1998; European Union Directive 1980/778/EEC, 1980; European Union Directive 1980/777/EEC, 1980). International standards have also been set by the World Health Organization (WHO, 1996, 2006) and the Food and Agriculture Organization (FAO, 1997). The WHO policy does not promote the adoption of international standards for drinking water quality, the main reason being the advantage provided by the use of a risk-benefit approach (qualitative or quantitative) in the establishment of national standards and regulations (WHO, 2006). The Romanian Law 311/2004 regulates drinking water quality, with the objective of protecting human health against any type of contamination of drinking water by providing clean water and its quality sanogenous.

The study of bottled waters represented an important objective of worldwide researchers, trying to characterize them from different points of view, by using different analytical techniques (Abouleish, 2012; Falcone-Dias et al., 2012; Moazeni et al., 2012; Igbeneghu and Lamikanra, 2014; Rey-Salgueiro et al., 2013).

Abouleish (2016) considered that increased dependence on bottled water over the world, demands high quality, which is very important by monitoring levels of minerals and pollutants, in order to increase consumers' confidence in its quality.

For identification of bottled waters origin, strontium and oxygen isotopes were used in some studies. Kim et al. (2013) investigated bottles waters from South Korea using $^{87}Sr/^{86}Sr$ ratio and isotope $\delta^{18}O$. The $^{87}Sr/^{86}Sr$ ratios ranged widely from 0.70503 to 0.75589 and the latitude effect on the isotope values was directly related to strontium ratios, with a negative correlation between them. Misund et al. (1999) used inductively coupled plasma atomic emission spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS), and ion chromatography techniques to analyzed 56 European bottled waters, with wide spread in the chemical composition that are due to geological environment or local regulations. Bakırdere et al. (2013) determined three toxic metals in tap and bottle waters using graphite furnace atomic absorption spectroscopy system. Bouvier-Capely et al. (2014) proposed a procedure for separation and preconcentration of uranium (U) from drinking waters using a combination of a specific column called AQUALIX with ICP-MS technique. U concentration for French bottled waters range from 0.08 to 2.1 μg L^{-1}. Some researches (Peters et al., 2015) characterized tap and bottled waters from Beijing, China for reporting the ability of these waters to serve as a safe drinking water source from the trace elements point of view. Multiple stable isotope analyses were used ($\delta^{15}N_{nitrate}$, $\delta^{18}O_{nitrate}$, $\delta^{34}S_{sulfate}$, $\delta^{18}O_{sulfate}$, and $\Delta^{33}S_{sulfate}$) on Beijing tap water for the identification of specific pollution sources. Gómez-Nieto et al. (2015) developed a high-resolution continuum source flame atomic absorption spectrometry method for fast sequential multielemental analyses. They used high-resolution continuum source flame atomic absorption spectrometry to determine 11 elements from drinking waters.

5.2 Macro-, Micro-, and Toxic Elements in Waters

There is a requirement for the bottling companies to label natural mineral waters with their characteristic chemical composition; most bottled waters are labeled with major-ion and basic physical characteristics. However, the concentrations of trace elements are rarely provided.

Analytical methods capable to detect low concentrations are necessary to determine trace elements in drinking water (bottled mineral and tap water). ICP-MS is an adequate technique for multielement determinations at low metal concentrations due to its low detection limit, precision, and wide linear dynamic range (Chajduk and Polkowska-Motrenko, 2017).

Drinking mineral water rich in magnesium sulfate and sodium sulfate can confer significant benefits for healthy digestion (Bothe et al., 2017). Potassium (K) is the most abundant positively charged electrolyte inside cells, being very important for the muscle contractility, including cardiac muscle (European Food Safety Authority (EFSA), 2006). Calcium (Ca) and magnesium (Mg) play an important role in the human organisms, Ca can prevent hypertension and osteoporosis and Mg may help to stabilize the electric cardiac system (Reinhardt, 1991).

According to the EU mineral water directives (80/777/EEC, 1996 and 2003/40/EC, 2003), bottled waters may be classified as: "containing calcium" with calcium content > 150 mg L^{-1}, "containing magnesium" with magnesium content > 50 mg L^{-1}, "containing sodium" with sodium content > 200 mg L^{-1}, and "suitable for low sodium diet" with sodium content < 20 mg L^{-1}. Customers buying bottled water also pay great attention to the sodium content of water, as this element seems to be associated with hypertension and coronary heart disease for some people (Cogswell et al., 2016). Sodium-bearing mineral water can help persons with blood pressure that is too low; it can also be used to treat acidic stomach problems (Käss and Käss, 2008). The estimated minimum daily requirement of Na for an adult is 500 mg, while the maximum intake, according to the recommended dietary allowance (RDA) is 2400 mg/day (US Food and Drug Administration, 2009). The results from element concentration point of view can be used to estimate ingestion amounts of certain elements by consumers. According to some authors (Azoulay et al., 2001), adult humans between ages 19 and 50 years require daily 1000 mg Ca^{2+}, 310–420 mg Mg^{2+}, and 2400–3000 mg Na^{+}.

The concentrations range for the major ions presented in a study made on 70 bottled water brands from Turkey (Güler and Alpaslan, 2009) were (in mg L^{-1}): 0–50.9 for Ca, 0.1–19.0 for Mg, 0.1–76.8 for Na, and 0.1–76.8 for K. By drinking 2 L of these bottled waters (per day), adult humans may fulfill only ~3% of their Ca^{+2} dietary reference intake (DRI) and between 2% and 1.5% and 0.7%–0.6% of their Mg^{+2} and Na DRI, indicating that most people may be consuming improper levels of Ca^{+2}, Mg^{+2} with important health consequences. The authors suggested that the customers must choose bottled water brands with optimal mineral content to prevent unfavorable health effects. Also, according to them, bottled water is not necessarily safer than tap water.

The data sets on Slovenian bottled waters available on the market from 2 years 2004 and 2008 presented median values for major ions (in mg L^{-1}): 65.6 (2004) and 76.4 (2008) for Ca; 1.45 (2004) and 0.9 (2008) for K, 32.4 (2004) and 34.9 (2008) for Mg, and 9.3 (2004) and 4.0 (2008) for Na (Brenčič et al., 2010).

Many elements, even major ones, determined for eight water brands sold in Cameroon market, presented very large natural variations that reflected local geological setting (Oyebog et al., 2012). Thus, the concentration range for the major ions (in mg L^{-1}) was: 0.67–57.9 (with a median of 19.15) for Ca, 0.32–18.54 (with a median of 11.86) for Mg, 0.19–9.18 (with a median of 4.46) for K, and 1.45–43.94 (with a median of 10.64) for Na. The dominant chemical types of the bottled water brands are Ca-HCO_3, Ca-Mg-HCO_3, Ca-Na-Mg-HCO_3, Na-HCO_3, and Na-Mg-HCO_3.

Sixteen mineral bottled waters of Sicilian brands were analyzed and chemically they range from Ca-HCO_3 and Ca-SO4 to Na-HCO_3 types (Varrica et al., 2013). The concentrations range of major ions was (in mg·L^{-1}): 5.39–85.3 for Ca, 2.67–24.9 for Mg, 0.8–8.38 for K, and 5.7–41.9 for Na. These results were compared with results from a study of 294 European bottled waters (Reimann et al., 2010) and 178 samples of bottled mineral waters from different Italian brands (Dinelli et al., 2012). The median values of studied waters were (in mg L^{-1}): 33.8 for Ca and 6.33 for Mg (lower than median value of European waters of 106 and 22.2 and Italian waters of 41.7 and 8.4) and 2.11 for K and 17.0 for Na (between median value of European waters of 2.5 and 18.05 and Italian waters of 1.2 and 7.4). Even if there were differences between the concentrations of bottled waters and of public waters supply, the authors consider that there are not sufficient reasons to prefer bottled waters unless there is some specific nutritional and health concerns.

A recent study made by Qian (2018) consider that the European bottled waters have higher levels of Ca and Mg than waters from other continent, because the bedrocks are younger and contain more from these elements. The same author shows that for the Swedish bottled waters, the content of Na and K is very high, being harmful for human health, especially for people with risk of cardiovascular diseases.

A survey of the inorganic chemistry of 85 bottled mineral waters from England was made by Smedley (2010). The concentrations of the most elements were appreciably lower, in some cases by one or two orders of magnitude. The concentrations of manganese (Mn) varied from <0.01 to 17.2 μg·L^{-1}. Exposure to Mn via contaminated drinking water is increasingly associated with adverse neurological outcomes, for example, exposure to Mn—contaminated well water is associated with increased infant mortality (Saritha et al., 2014). Therefore, for safety reasons, the Canadian Pediatric Society does not recommend bottled water for infant consumption (Joint Working Group et al., 1998). Barium (Ba) is a naturally present constituent, in mineral and spring waters and the maximum admissible level in natural mineral waters and natural spring waters was imposed at 0.7 mg L^{-1} (WHO, 2006). The concentration of Ba in these analyzed bottled waters were between <2 and 1010 μg L^{-1}, two of them having a value above the natural mineral limit. Due to the adverse health effects of arsenium (As), the measurement at trace level of this element in any samples related with human being is very important (Bakırdere et al., 2013). A total of 88% from the bottled waters are As concentration lower than 2 μg·L^{-1}, less than half the European and national drinking-water limit of 10 μg L^{-1}.

Birke et al. (2010) analyzed 71 elements in the German bottled and tap water samples by different methods, a wide range of concentrations being found for most of the elements analyzed. Less analyzed elements determined are, for example, silicium (Si), boron (B), lithium (Li), tellurium (Te), and beryllium (Be). Si and B concentrations were between 0.94 and 40.50 and 0.002–2.61 mg L^{-1} in bottled water and between 1.17 and 20.10 and 0.003–0.25 mg L^{-1} in tap water. Li, with similar behavior to Na, was found in the range of concentration between 0.0005 and 2.79 mg L^{-1} in bottled waters and between 0.0002 and 0.074 in tap water. Be and Te are toxic metals, the first can cause toxic and hypersensitive reactions in the skin (Rossmann, 2000) and the second produces a sharp garlic odor of the breath and a metallic taste in the mouth (Kobayashi, 2004). Be and Te concentrations in bottled waters vary between 0.001 and 7.30 μg L^{-1} and 0.005–0.21 μg L^{-1}, while in the tap waters between 0.001 and 0.2 μg L^{-1} and 0.005–0.025 μg L^{-1}.

Temperature-dependent leaching of chemical elements from mineral water bottle materials was studied by Reimann et al. (2012) in 40 mineral waters bottles from Europe markets. There were tested waters from blue, green, and clear glass bottles and for comparison, polyethylene terephthalate bottles. The concentration of lead (Pb) in glass bottles was higher than in polyethylene terephthalate recipients for all temperatures. A strong increasing of Pb content was observed in clear glass bottles with temperature and a small one in blue and green glass bottles. Antimony (Sb) was the only element that shown different behavior in glass and plastic recipients, being in high concentrations in the last category. The content of this element increases in waters for both bottles materials and for all colors.

Felipe-Sotelo et al. (2015) compared the chemical composition of 37 bottled waters from the United Kingdom and Continental Europe. British waters generally showed lower levels of most elements. For example, Mo, Sb, or Cd which is highly toxic and responsible for several cases of poisoning through food (Komorowicz and Barałkiewicz, 2016). The range concentrations of zinc (Zn) in all tested waters were 0.178–83.0 μg L^{-1}, with a mean value of 5.55 μg L^{-1}. This metal is considered to be an antioxidant, acting as catalyst or stabilizing protein structure (Silvera and Rohan, 2007; Altun et al., 2017). No limit exists currently for Zn in European drinking water. Waters from Czech Republic and Slovakia presented the highest concentrations of Pb, these from Germany showed the highest concentration of Ni and Mn, while Italian bottled waters exhibited the highest levels of Sr. This element can be toxic when consumed in too high amounts; strontium impairs mineralization of the bone which is attributed to osteomalacia and rickets (Swer et al., 2016). It was reported that a Ca/Sr ratio < 100 in drinking water in one region of Russia caused a high incidence of osteoporosis (increased fragility of bones) (Yudakin and Malov, 2008). In Romania, there is no defined standard for Sr in water; Russia, for example, has a limit of 7 mg L^{-1} Sr for bottled water, but the studied bottled water samples had concentration under the Russian limit (Birke et al., 2010).

Trovoa et al. (2017) developed a method for the determination of vanadium (V) in water samples from hydromineral spa and bottled waters from Brazil, using ICP-MS technique. According to the authors, there is a contemporary medicinal interest in vanadium, due to its relationship to insulin levels and its use in drugs for diabetes, so it is very important to monitor the concentration of this element because people ingest the waters for medical purposes (Cornelis et al., 2005). The concentration of this metal ranged from 65.2 to 831 μg L^{-1}.

Rahman et al. (2017) determined a total of 24 elements in 14 different brands of drinking waters from Bangladesh market. They found a high content of Al, over the permissible limit, while the concentration of Pb is not significantly different from the guideline values. These waters had better quality from Pb contamination or microbial hazard point of view than tap waters.

Regarding the trace metal contents, to evaluate the overall quality of drinking waters, some authors (Tamasi and Cini, 2004) proposed an index which takes into account possible unhealthy additive effects. This metal index (MI) is based on the largest possible number of trace metals and was defined as (Eq. 5.1):

$$\mathrm{MI} = \sum_{i=1}^{M} \frac{C_i}{(\mathrm{MAC})_i} \tag{5.1}$$

where C is the concentration of each element in solution, i is the ith sample, and MAC is the maximum allowed concentration. The higher the concentration of a metal compared to its respective MAC value, the worse the quality of the water is. If the concentration of a certain element is higher than the respective MAC value ($\mathrm{MI} > 1$), the water cannot be used according to the law, waters with MI values exceeding 1 are beyond an indicative warning threshold. The presence of several elements with concentrations smaller than but close to the respective MAC values will also decrease the overall quality of water because of an additive effect. Thus, an MI value > 1 is a threshold of warning, even in the case where $C_i < \mathrm{MAC}_i$ for all the elements.

5.3 Isotopic Characterization of Drinking Waters

The natural isotopic composition of hydrogen and oxygen can be used to the authentication of bottled water origin (Bowen et al., 2005; West et al., 2014). From microbiological assay results, a mineral water must be pure water, having groundwater origin and coming from a reservoir or aquifer and it is exploited by natural emergences or wells.

Groundwaters keep the isotopic fingerprint of their origin overtime, even 10,000 years, insured they are not exposed to temperatures over 60–80°C (Gat, 1981). The isotopic values (δ^2H and $\delta^{18}O$) of fresh water range widely across the planet as a consequence of the spatially and temporally variable climatic conditions which govern the quantity of precipitated water to geographic regions (Giustini et al., 2016). Changes in δ^2H and $\delta^{18}O$ values occur with an increase in latitude, altitude, and continentally (Bowen et al., 2005).

Although a number of studies have examined various types of bottled water, including still and sparkling water, using stable isotopes (^{18}O and ^2H) or chemical elements, few studies have combined both types of determinations.

Raco et al. (2013) had investigated the stable isotope composition for 52 samples of Italian bottled waters. The isotope ratios of hydrogen and oxygen for Italian bottled waters occur within a range of typical meteoric waters values, from −99‰ to −36‰ for δ^2H, and respectively from −13.8‰ to −5.05‰ for $\delta^{18}O$. In addition, the isotope ratio of carbon was measured in the dissolved inorganic carbon (DIC) from carbonated bottled waters, in order to check the CO_2 origin in these samples, natural or synthetic. The most negative values obtained for $\delta^{13}C$ were associated with exogenous CO_2. Another isotopic study regarding the bottled water was made by Brencic and Vreca (2010) for 74 samples, Slovenian and foreign. Beside δ^2H, $\delta^{18}O$, and $\delta^{13}C_{DIC}$ values determined, the authors used, as novelty, statistical methods to determine a finite mixture of probability distribution in order to characterize and authenticate the water samples. Dotsika et al. (2010) investigated, from stable isotopes point of view, Hellenic bottled waters. Stable isotope composition varied for all samples, summing 25 still waters, between −9.9‰ and −6.9‰ for $\delta^{18}O$, and between −67.5‰ and −46.5‰ for δ^2H. These values have no relevance to health, but they are very useful instruments in quality control and, also, for establishing the bottled waters origin. These authors compared the isotopic fingerprint of Greek still waters with that of natural spring water, demonstrating that the isotopic signature of bottled waters keeps data about water sources from them originated.

Bowen et al. (2005) studied 234 samples of bottled waters collected worldwide, by using isotope ratio mass spectrometry (IRMS). These data can be used in different applications fields, from regulatory to forensic domain. Hydrogen isotopic value varied from −147‰ to 15‰, and oxygen isotopic composition from −19.1‰ to 3‰, being in the normal range of meteoric waters. Two case studies, from this paper, showed that transport of bottled waters can conduct to important differences between the isotopic fingerprint of bottled waters and of environmental water at the acquisition location.

Bong et al. (2009) combined both, stable isotope composition and chemical profile, to study the bottled waters from South Korea market, totalizing 50 samples from 35 brands, divided into three categories: still water, sparkling water, and marine water. The pH obtained for still waters ranged between 6.73 and 10.10, for sparkling samples was in the interval 5.60–6.70 and 6.38–7.40 for water of marine origin, respectively. The authors obtained the most elevated average concentrations for macroelements from sparkling water samples. The isotopic composition of oxygen and hydrogen varied from −15.7‰ to −6.4‰ and −120.6‰ to −41.3‰ for still waters. The isotopic values were different for sparkling and marine water samples. Thus, $\delta^{18}O$ ranged from −12.75‰ to −6.32‰ and −10.30‰ to −0.05‰, respectively; and $\delta^{2}H$ from −91.5‰ to −41.8‰ and − 64.5‰ to −1.7‰, respectively. By using statistical analysis combined with both analytical techniques, the authors obtained better discrimination of water types and bottled waters origin.

5.4 Data Processing Using Chemometric Methods

The progresses that were made in the field of analytical techniques, allow the measurement of a large number of samples, which is required especially in the food or beverages area. Moreover, for an efficient characterization of a matrices, a large number of samples is mandatory, because otherwise that specific matrices would not been fully represented. Along with this advantage offered by analytical techniques, arise the problem of data results interpretation. This "inconvenient" might be solved by applying different chemometric techniques, which may allow a visual insight of data variation or may highlight some information, that otherwise would not have been discovered. Another advantage brought by chemometric methods is that allow the interpretation of coupled experimental results from different analytical techniques, fact that permit a more comprehensive classification. A first step in the chemometric approach of experimental data, is finding the suitable analysis that can extract the best valuable results, because not all statistical tests are suitable for all experimental data set. In some cases, there are specific test that must be run before chemometric itself, which must satisfy certain criteria. The heaviest step and also the key step, is the interpretation of results obtained after chemometric processing, because sometime a simple analysis can generate a large number of tables and graphical representation. For example, when elemental content is analyzed in a specific matrix, some association between elements and sample, might not be satisfactory, as results interpretation. A step forward might be represented by identification of sources that generate that specific elemental content (Lees, 2003).

Among chemometric techniques, the most widely used is analysis of variance (ANOVA) and principal component analysis (PCA), which provide the possibility to systematize the obtained data from different analytical techniques (Kruzlicova et al., 2013), or might be used in order to investigate the differentiation of selected samples with respect to different criterions. ANOVA is preliminary step for identification of parameters that are statistically contributing to the data sets variability, providing information on the differences among different sample under discussions.

PCA aims in the reduction of dimension of original data matrix by retaining the maximum amount of variability (Otto, 2017). Before carrying out the PCA two important tests were made: Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy and Bartlett's test of sphericity. The KMO statistic varies between 0 and 1 (Miller and Miller, 2010).

The study reported by Kraic et al. (2008) presented the analysis and classification of potable, spring, and mineral water. They analyzed a number of 93 water sample, from four different countries. The obtained results were processed using different chemometric techniques such: PCA, cluster analysis, linear and quadratic discriminant analysis, correlation analysis, and ANOVA. By applying ANOVA, it was revealed that three water types were separated only by ^{121}Sb and ^{123}Sb, while ^{111}Cd, ^{114}Cd, ^{208}Pb, ^{47}Ti, ^{56}Fe, ^{63}Cu, and ^{66}Zn could be used to differentiate tap water group from the spring and mineral water group. The same study on drinking water, reported the results using PCA as chemometric method applied for data set dimensionally reduction. It was pointed out that Sr, Li, B, Ni, Co, As, ^{121}Sb, ^{123}Sb, ^{118}Sn, ^{120}Sn, Tl, Be, and Cr, presented large values for both extracted component, fact that make them suitable characteristics for some types of water samples.

Another published paper reported the characterization of 132 samples of mineral water from physicochemical and compositional point of view. By applying PCA, a percent of 87% from data set variability was explained, using the first three principal components obtained. The first component represented the water hardness, the second component was associated with origin of water, while the third one was attributed to the salinity of analyzed samples (Versari et al., 2002).

A more recent study was conducted on a sample set having 20 samples. The aim was to highlight the most important physicochemical parameters which are responsible for water flavor, using chemometric techniques. It was highlighted that residual chlorine is a parameter that might discriminate between tap and bottle water PCA and linear discriminant analysis (LDA) confirmed that chemometric techniques represent a useful approach for evidencing taste of tap and mineral water samples (Platikanov et al., 2013).

5.5 Elemental and Isotopic Content, Combined With Chemometric Approach, for Romanian Mineral Water Characterization

Two analytical techniques are employed for investigation of chemical characteristics of the most widely distributed domestic brands of bottled waters on Romanian market. These analytical techniques are: ICP-MS and IRMS, along with chemometric methods, used for results interpretation.

To our knowledge, for Romanian bottled waters there are no studies concerning stable isotope ratios and microelements, together with chemometric approach. But, some studies focused on similar matrices exist. For example, Fan et al. (2017) or Geana et al. (2013) analyzed wine samples using the elemental profile [inductively coupled mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES)], IRMS, and chemometric analysis, with the aim of discrimination three geographical origins. Voica et al. (2015) used the same analytical methods for characterization of beer samples, the trace elements, and isotopic content being used further for chemometric processing. A comparison of the beers quality bottled in the different type of packaging like glass, dose, PET was made.

Another matrices studied by combining isotopic and elemental content of samples together with chemometric methods included: food products—vegetables (Cristea et al., 2017a; Magdas et al., 2017; Feher et al., 2017), milk (Magdas et al., 2017), and medicines (Cristea et al., 2017b), highlighting the importance of IRMS and ICP-MS techniques corroborated by statistical methods in origin product identification, quality control, and false statements of food provenance.

A total of 24 brands of bottled waters, summing 29 samples, were investigated. From total, 25 samples, commercially available on Romanian market, were purchased randomly in 2012 and 2013 from local supermarkets and independent food stores. Four foreign samples (from Turkey, Canada, and Israel) were collected in 2012 and 2013 through personal purchases and solicitation of colleagues. Information on the sampling location and origin of the bottled water was taken from the bottle labels, when indicated. The bottled water was divided into two groups based on its origin: still water (water without the presence of dissolved gaseous CO_2), and sparkling water (water in which dissolved gaseous CO_2 was present).

5.5.1 Element Determination

Analyses for total concentrations of macro minerals like Ca, Mg, Na, and K, trace elements like Mn, Ni, Zn, Cu, Ba, Al, Sr, Co, and V, and toxic metals like Cd, Pb, and As were carried out by inductively coupled plasma quadrupole mass spectrometry. A PerkinElmer ELAN DRC (e) instrument was used with a Meinhard nebulizer and silica cyclonic spray chamber and continuous nebulization. The DRC is an advanced ICP-MS system that uses dynamic reaction cell technology to eliminate interferences. DRC technology places a pressurized, closed cell between the ions lens and the analyzer quadruple in an ICP-MS.

The accuracy (as recovery) and precision [as relative standard deviation (RSD)] of the analytical technique was evaluated by analyzing a certified standard reference material. A high-purity inductively coupled plasma multielement standard solution from Perkin Elmer Life and Analytical Science used for the calibration curve in the quantitative analysis (acceptable for $R > 0.999$), was a mixture of 10 mg L^{-1} of Na, Ca, Mg, K, Al, Mn, Ni, Cu, As, Sr, Cd, Ba, Pb, V, and Co. The detection limits (ng L^{-1}) were: 1.1 for Cd, 0.5 for Pb, 2.6 for Mn, 1.2 for Ni, 4.6 for Zn, 3.5 for As, 1.3 for Cu, 1.7 for Al, 0.9 for Ba, 0.5 for Sr, and 2.2 for V. The RSDs ranged from 0.6% to 6.4% confirmed the high precision of the method.

The range of macroelements concentrations was: Na: 0.59–446.8 mg L^{-1} (a mean of 59.281 mg L^{-1}); Mg: 0.89–189.45 mg L^{-1} (a mean of 29.968 mg L^{-1}); K: 0.032–42.17 mg L^{-1} (a mean of 4.148 mg L^{-1}); and Ca: 5.41–293.7 mg L^{-1} (a mean of 55.968 mg L^{-1}). It was observed that the Ca content has higher values for the mineral sparkling waters than for the still waters. According to the EU classification (80/778/EEC and 2003/40/EC), 13.8% of the analyzed bottled water may be classified as "containing calcium," 17.2% as "containing magnesium," and 6.8% as "containing sodium." From the analyzed mineral water samples, 51.7% were "suitable for low sodium diets." In order to estimate ingestion amounts of certain elements by consumers, for the bottled waters examined in this study, adult humans may fulfill only ≈ 6.2% of their Ca^{2+} DRI, between 8.5% and ≈ 12% of their Mg^{2+} DRI and between only 2.1% and 2.7% of their Na^{+} DRI by drinking 1.5 L of bottled water per day (the calculations were made using mean values).

Trace element composition of studied bottled waters was characterized and the results are presented in Table 5.1. The concentrations range for some of the studied elements was (in μg L^{-1}): < 0.001–0.077 for Cd; < 0.001–0.067 for Pb; < 0.001–305.608 for Mn; 0.222–10.520 for Ni; < 0.001–13.908 for Zn; < 0.001–58.778 for Al; 0.092–1.231 for As; 0.128–4.247 for Cu; 0.072–3.291 for Co; 0.046–10.998 for V; and 0.892–724.726 for Ba.

These results aim to assess the compliance of Romanian bottled water brands to several standards around the world including European Community Council Directive 98/83/EC (EC, 1998) and WHO guideline values (WHO, 2006). Even though the Mn average value of 37.61 μg L^{-1} is far below of the European guideline value of

Table 5.1 Metal Content in Studied Waters (Mean ± SD)

Water Code	Metal Concentration (μg L^{-1})											
	Cd	**Pb**	**Mn**	**Ni**	**Zn**	**Al**	**As**	**Cu**	**Co**	**V**	**Ba**	**Sr**
WA$_1$	0.002 ± 0.0004	0.009 ± 0.0004	0.525 ± 0.036	0.923 ± 0.057	0.005 ± 0.013	1.558 ± 0.103	0.666 ± 0.014	0.196 ± 0.017	2.611 ± 0.040	0.094 ± 0.027	12.066 ± 0.541	55.098 ± 4.811
WA$_2$	0.004 ± 0.0004	0.001 ± 0.001	0.100 ± 0.020	0.605 ± 0.015	0.257 ± 0.024	1.670 ± 0.430	0.456 ± 0.022	0.165 ± 0.019	2.149 ± 0.311	0.435 ± 0.007	3.813 ± 0.419	33.472 ± 2.722
WA$_3$	0.004 ± 0.0004	0.002 ± 0.001	0.310 ± 0.13	1.011 ± 0.066	0.477 ± 0.032	3.558 ± 0.677	0.131 ± 0.003	0.334 ± 0.004	2.548 ± 0.093	0.091 ± 0.009	19.318 ± 0.415	228.945 ± 17.853
WA$_4$	0.020 ± 0.007	0.017 ± 0.001	0.580 ± 0.025	0.514 ± 0.045	2.211 ± 0.130	1.018 ± 0.033	0.237 ± 0.033	0.152 ± 0.003	0.310 ± 0.004	3.937 ± 0.057	2.722 ± 0.156	35.675 ± 3.136
WA$_5$	< 0.001	0.001 ± 0.0001	< 0.001	0.609 ± 0.055	0.097 ± 0.054	< 0.001	0.939 ± 0.015	0.128 ± 0.017	1.278 ± 0.061	0.306 ± 0.004	16.269 ± 0.084	58.660 ± 3.228
WA$_6$	0.005 ± 0.0002	< 0.001	0.105 ± 0.009	0.222 ± 0.025	0.679 ± 0.104	4.122 ± 0.822	0.206 ± 0.007	0.229 ± 0.004	0.354 ± 0.027	2.465 ± 0.040	0.923 ± 0.091	58.436 ± 2.867
WA$_7$	0.054 ± 0.006	0.006 ± 0.003	128.565 ± 4.936	0.797 ± 0.086	1.391 ± 0.114	2.325 ± 0.124	0.301 ± 0.031	3.355 ± 0.042	0.144 ± 0.047	0.160 ± 0.014	112.616 ± 25.014	645.840 ± 59.632
WA$_8$	0.009 ± 0.001	< 0.001	0.081 ± 0.090	0.951 ± 0.009	0.067 ± 0.012	26.689 ± 6.810	0.140 ± 0.024	0.176 ± 0.001	2.030 ± 0.225	0.119 ± 0.022	85.115 ± 1.737	250.977 ± 20.112
WA$_9$	0.007 ± 0.0008	0.004 ± 0.001	1.680 ± 0.298	0.914 ± 0.006	0.185 ± 0.044	< 0.001	0.291 ± 0.028	0.219 ± 0.001	3.011 ± 0.001	1.132 ± 0.022	11.506 ± 0.600	128.445 ± 10.778
WA$_{10}$	0.003 ± 0.001	0.001 ± 0.003	0.284 ± 0.055	1.047 ± 0.052	0.242 ± 0.036	0.636 ± 0.058	0.235 ± 0.017	0.240 ± 0.001	2.631 ± 0.416	0.333 ± 0.029	6.617 ± 0.803	43.686 ± 2.853
WA$_{11}$	0.026 ± 0.006	< 0.001	0.064 ± 0.028	0.360 ± 0.015	5.713 ± 0.323	22.018 ± 2.626	0.092 ± 0.010	0.142 ± 0.001	0.902 ± 0.029	0.095 ± 0.006	20.326 ± 0.840	12.029 ± 0.578
WA$_{12}$	0.004 ± 0.001	0.001 ± 0.0002	0.055 ± 0.002	1.083 ± 0.012	0.682 ± 0.056	< 0.001	0.334 ± 0.010	0.236 ± 0.066	2.618 ± 0.350	0.388 ± 0.006	17.508 ± 0.60	54.783 ± 5.455
WA$_{13}$	0.005 ± 0.0003	0.004 ± 0.001	0.920 ± 0.550	0.362 ± 0.017	0.159 ± 0.017	< 0.001	0.433 ± 0.015	1.103 ± 0.062	0.137 ± 0.027	0.940 ± 0.065	170.142 ± 6.330	561.056 ± 47.321
WA$_{14}$	0.024 ± 0.006	0.011 ± 0.003	0.800 ± 0.073	1.098 ± 0.084	0.337 ± 0.030	10.577 ± 2.716	0.469 ± 0.042	1.339 ± 0.129	0.728 ± 0.029	1.125 ± 0.098	145.331 ± 5.376	279.126 ± 15.443
WA$_{15}$	0.029 ± 0.003	0.018 ± 0.003	0.498 ± 0.028	4.548 ± 0.220	12.624 ± 0.493	1.989 ± 0.517	0.859 ± 0.038	1.166 ± 0.052	2.605 ± 0.382	0.613 ± 0.022	135.433 ± 4.571	942.91 ± 85.663
WA$_{16}$	0.027 ± 0.009	0.010 ± 0.003	0.216 ± 0.019	1.462 ± 0.340	4.596 ± 0.141	< 0.001	1.231 ± 0.102	1.084 ± 0.022	2.041 ± 0.438	10.998 ± 0.138	105.047 ± 2.278	239.22 ± 19.002
WA$_{17}$	0.012 ± 0.0006	0.049 ± 0.002	305.608 ± 12.830	1.630 ± 0.081	0.951 ± 0.079	0.579 ± 0.016	0.723 ± 0.001	4.247 ± 0.153	0.506 ± 0.077	0.744 ± 0.059	178.751 ± 4.70	206.52 ± 15.212
WA$_{18}$	0.005 ± 0.0006	0.005 ± 0.001	0.283 ± 0.034	0.390 ± 0.009	0.449 ± 0.041	< 0.001	0.151 ± 0.038	1.206 ± 0.093	0.072 ± 0.007	0.200 ± 0.004	27.996 ± 1.307	202.59 ± 15.778
WA$_{19}$	< 0.001	0.001 ± 0.0004	0.013 ± 0.009	0.330 ± 0.006	< 0.001	0.236 ± 0.088	0.140 ± 0.042	0.733 ± 0.017	0.350 ± 0.025	0.046 ± 0.009	78.249 ± 1.118	74.07 ± 6.090
WA$_{20}$	0.013 ± 0.006	0.018 ± 0.006	0.187 ± 0.081	2.027 ± 0.116	3.430 ± 0.132	0.949 ± 0.081	0.649 ± 0.071	0.581 ± 0.025	1.372 ± 0.379	0.160 ± 0.013	128.198 ± 31.659	147.09 ± 12.958
WA$_{21}$	0.003 ± 0.0004	< 0.001	0.133 ± 0.037	0.526 ± 0.013	0.631 ± 0.035	7.698 ± 0.965	0.247 ± 0.015	0.137 ± 0.013	0.931 ± 0.019	7.116 ± 0.090	3.506 ± 0.243	31.06 ± 2.114
WA$_{22}$	0.005 ± 0.0003	< 0.001	0.105 ± 0.029	0.902 ± 0.079	1.695 ± 0.146	3.424 ± 0.878	0.270 ± 0.037	0.230 ± 0.008	1.047 ± 0.051	7.105 ± 0.264	3.468 ± 0.660	31.12 ± 1.996
WA$_{23}$	0.010 ± 0.001	0.017 ± 0.002	25.457 ± 0.967	8.040 ± 0.323	1.404 ± 0.139	< 0.001	0.477 ± 0.075	3.323 ± 0.140	0.867 ± 0.020	0.540 ± 0.014	0.892 ± 0.056	4177.15 ± 258.771
WA$_{24}$	0.002 ± 0.0002	0.013 ± 0.001	0.408 ± 0.088	3.225 ± 0.124	1.091 ± 0.108	< 0.001	0.126 ± 0.043	1.054 ± 0.030	0.505 ± 0.052	0.129 ± 0.004	138.191 ± 4.141	2234.61 ± 175.035
WA$_{25}$	0.077 ± 0.009	0.024 ± 0.008	257.488 ± 10.215	10.520 ± 0.233	2.439 ± 0.197	< 0.001	0.265 ± 0.013	0.617 ± 0.017	3.291 ± 0.281	0.091 ± 0.007	172.488 ± 7.854	4042.07 ± 300.551
WA$_{26}$	0.002 ± 0.0006	0.008 ± 0.001	3.180 ± 0.121	5.453 ± 0.116	4.180 ± 0.207	0.606 ± 0.016	0.404 ± 0.025	0.480 ± 0.013	1.381 ± 0.187	1.241 ± 0.015	59.513 ± 0.393	1794.99 ± 168.442
WA$_{27}$	0.018 ± 0.006	0.040 ± 0.008	209.757 ± 9.263	10.809 ± 0.436	6.157 ± 0.285	0.577 ± 0.042	0.810 ± 0.034	1.405 ± 0.030	1.873 ± 0.200	0.265 ± 0.008	261.856 ± 6.553	1970.29 ± 180.443
WA$_{28}$	0.006 ± 0.0009	0.017 ± 0.008	152.087 ± 6.881	5.444 ± 0.108	0.686 ± 0.025	58.778 ± 4.970	0.697 ± 0.051	1.660 ± 0.036	0.876 ± 0.056	3.670 ± 0.167	724.726 ± 19.546	1921.91 ± 167.070
WA$_{29}$	0.085 ± 0.008	0.067 ± 0.011	1.363 ± 0.275	0.733 ± 0.119	13.908 ± 3.806	5.248 ± 0.270	0.272 ± 0.026	0.358 ± 0.058	0.818 ± 0.019	0.119 ± 0.012	19.515 ± 0.735	55.57 ± 4.890
EC Directive	*5*	*10*	*500*	*20*	–	*200*	*10*	*2000*	–	–	*700*	–
WHO Directive	*3*	*10*	*400*	*70*	–	–	*10*	*2000*	–	–	–	–
Romanian Directive	*5*	*10*	*50*	*20*	*5000*	*200*	*10*	*100*	–	–	–	–

SD, standard deviation.

500, respectively, 400 μg L^{-1}, five samples of bottled waters distinctly exceeded the concentration of 50 μg L^{-1} from Romanian Directive (Romanian Law 311/2004). The Mn concentrations for these waters are: 128.565, 305.608, 257.488, 209.757, and respectively 152.087 μg L^{-1}. All bottled waters have concentrations of Zn much below the value from Romanian guideline value for Zn in drinking water of 5 mg L^{-1}. Copper is the metal that was detected in all the samples, but there was no health-related risk. The Sr concentration in the analyzed bottled water lies between 0.012 and 4.177 mg L^{-1}.

From toxic elements point of view, concentrations of Pb and Cd in the bottled waters lie in the range < 0.001–0.067 μg L^{-1} and < 0.001–0.077 μg L^{-1}, below the European and National drinking-water limit of 10 μg L^{-1} for Pb and 5 and 3 μg L^{-1}, respectively, for Cd. Concentrations of As in the studied samples lie in the range < 0.092–1.231 μg L^{-1}, below the admissible limits.

The MI, used to evaluate the quality of waters based on 11 metals content, presented for two natural mineral waters and three mineral waters high values (2.86, 6.59, 5.97, 5.21, 4.73, and 4.02), clearly indicating low-quality water. These highest contributions to MI came from Mn and Ba.

5.5.2 Isotopic Determination

The $\delta^{18}O$ and $\delta^{2}H$ values in water were determined by using a liquid-water isotope analyzer (DLT—100, Los Gatos Research). The stable isotope values were expressed in delta (δ) notation (Brand et al., 2014):

$$\delta X = \left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \tag{5.2}$$

where X is the heavy isotope (^{2}H, ^{18}O), δ is in parts per thousand (‰) deviation relative to a standard gas, and R_{sample} and R_{standard} are the ratios of the heavy to the light isotopes for sample and standard, respectively. The isotopic compositions of ^{2}H and ^{18}O were expressed relative to international standard Vienna Standard Mean Ocean Water (V-SMOW). The limit of uncertainty of the isotopic analysis was ±0.2‰ for $\delta^{18}O$ and ± 0.6‰ for $\delta^{2}H$. Each sample was analyzed six times, but only the last three injections were taken into consideration for the calculations. A set of five internal standards was used, having $\delta^{18}O = -19.57$‰, -15.55‰, -11.54‰, -7.14‰ and -2.96‰, and $\delta^{2}H = -154.1$‰, -117.0‰, -79.0‰, -43.6‰, and -9.8‰, respectively.

The isotopic compositions of Romanian bottled waters ranged between -87.7‰ and -65.0‰ (average -73.57‰) for hydrogen, and between -12.92‰ and -9.15‰ (average -10.79‰) for oxygen, respectively. As it can be seen in Fig. 5.1, in the plot of $\delta^{2}H$ and $\delta^{18}O$ bottled water samples were clustered along the global meteoric

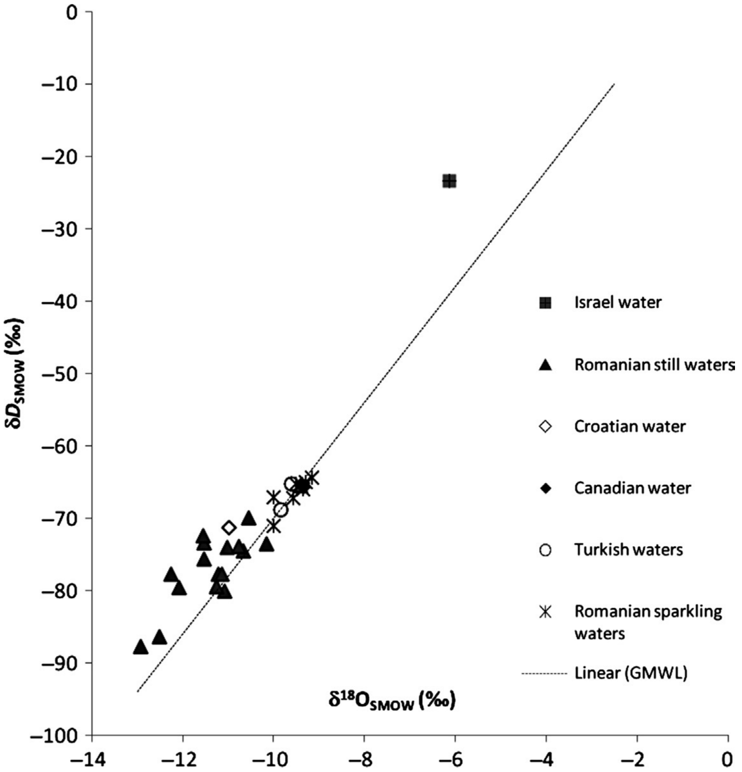

Fig. 5.1 The isotopic composition of studied water samples.

water line (GMWL, $\delta^2H = 8\times\delta^{18}O + 10$). The GMWL represents the global relationship between ^{18}O and ^2H in meteoric waters (Talabi, 2013). For each rain events, the precipitation samples were collected in Cluj-Napoca city (Transylvania, Romania) between January and December 2012 in order to build a local meteoric water line (LMWL). The obtained equation for LMWL from monthly averages weighted is $\delta^2H = 7.98\times\delta^{18}O + 9.8$. Our results suggest the fact that the δ^2H and $\delta^{18}O$ values of the bottled waters reflect a relatively satisfactory ANOVA source water signature (Bowen et al., 2005). The isotope composition of water varies greatly by temperature, latitude, altitude, and precipitation amount (Brencic and Vreca, 2006). Therefore, the oxygen and hydrogen isotope compositions of bottled waters preserve important information about the water source, production location, and natural processes in the hydrological cycle. The isotopic compositions of hydrogen and oxygen are higher for the sparkling waters than those for the still mineral waters. This shift in ^{18}O to higher values could be explained as a result of the nonconservative behavior of water in the aquifer through interaction with rock components which contain oxygen (Gat, 1981). For the foreign bottled waters, the isotopic values were quite similar between the sample from Canada (−65.7‰ δ^2H, −9.33‰ δ^{18}O) and one of the samples from Turkey (−65.3‰ δ^2H, −9.61‰ δ^{18}O). Instead, the sample from Israel had the most enriched values for hydrogen and oxygen, namely −23.5‰, and −6.12‰, respectively. This result is in accordance with Gat (1981) which has noted that under arid conditions, an enrichment of heavy isotope species in groundwater was observed. This fact could be explained as a result of evaporation processes.

5.5.3 Statistical Analysis

As it was stated earlier, the matrices used for chemometric processing might be composed of different parameters, obtained from different analytical techniques, in this specific case, ICP-MS and IRMS. The obtained results for 29 water samples were subjected to ANOVA test and PCA using IBM SPSS Statistics version 24. ANOVA analysis was performed for highlighting the elements that can distinguish Romanian waters from foreign one, or elements that differentiate mineral still water (MW) from natural SW. The differences were considered for $P < .05$ for 95% probability. PCA depicted a natural grouping of the studied samples, allowing a classification based on all measured variables, due to the fact that is unsupervised technique.

ANOVA was conducted separately for major elements (Na, Mg, K, Ca) and for trace and toxic elements (Mn, Ni, Zn, Al, Cu, Co, V, Ba, As, Cd, Pb) analyzed in every water samples. Regarding the comparison between water types, MW and SW: Na ($P = .001$), Mg ($P = .001$), Ca ($P = .001$) and by minor elements: Pb ($P = .003$). Ni ($P = .001$), Mn ($P = .047$), Ba ($P = .021$) could be used as differentiation markers for investigated types of water. The Romanian waters could be distinguished only by V ($P = .001$) from foreign ones.

PCA was applied to data set containing for trace and toxic elements (Mn, Ni, Zn, Al, Cu, Co, V, Ba, As, Cd, Pb) and major elements (Na, Ca, K, Ca) using the next parameters: extraction method was principal component, only components with eigenvalues > 1 were retained and Varimax was the appropriate rotation method. The value obtained for KMO test was 0.513, fact that indicates that PCA is suitable and the results could provide independent components. Bartlett's test measures the null hypothesis, being significant for P values < .05. The obtained value ($P = .001$) indicated that some relationships between variables exist and the PCA was appropriate.

The results indicated that six components had eigenvalues bigger than 1 (PC 1—4.843, PC 2—2.336, PC 3—1.636, PC 4—1.529, PC 5—1.251, PC 6—1.025). The first component explained 32.285% and was defined generally by major elements along with Ni. The following component (15.576% variance) was formed by same of toxic elements (Cd, Pb, and Zn), while the rest of parameters was grouped in other PCs. The Pearson correlation matrix (data not shown) presented values >0.5, which represented strong correlations between variables. Thus, a positive correlation means that, when a variable increases, correlated variables increase also, while a negative correlation means an increase in the primary variable causes a decrease in the correlated variables. Positive correlations were observed as follows: Ni with Na (0.594), Ni with Mg (0.725), Ni with Ca (0.954), Na with Mg (0.528), Na with Ca (0.538), and Ca with Mg (0.794). These elements appeared in first PC and are very strong correlated among them, fact that could be interpreted as a common source of provenience. The fact that all macroelements were very interestingly grouped in the first component proved that these elements dominate the water samples. Other correlations that should be mentioned are between elements that were found in the second component namely: Cd with Pb (0.598), Cd with Zn (0.612), and Pb with Zn (0.612).

The most important graphical representations obtained after PCA are represented by scores and loadings plot and it can be seen in Figs. 5.2 and 5.3. From the scores representation, it can be concluded that mineral waters might be distinguished very well from still waters and have different characteristic elemental content.

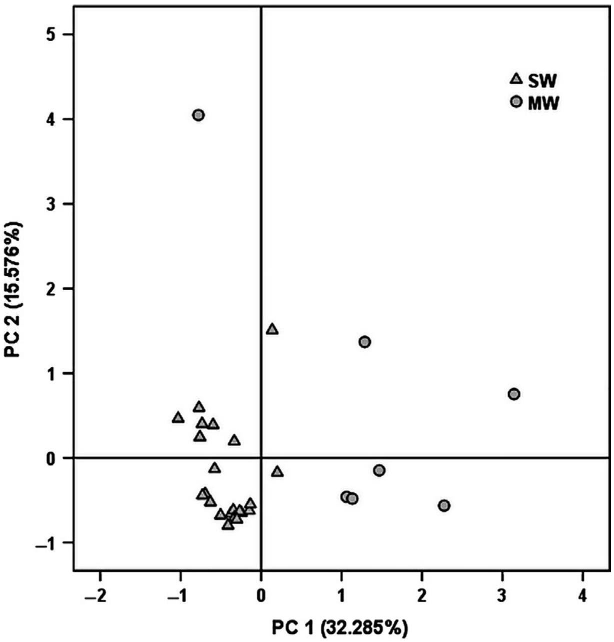

Fig. 5.2 Score plot of Romanian and foreign mineral waters obtained for minor elements.

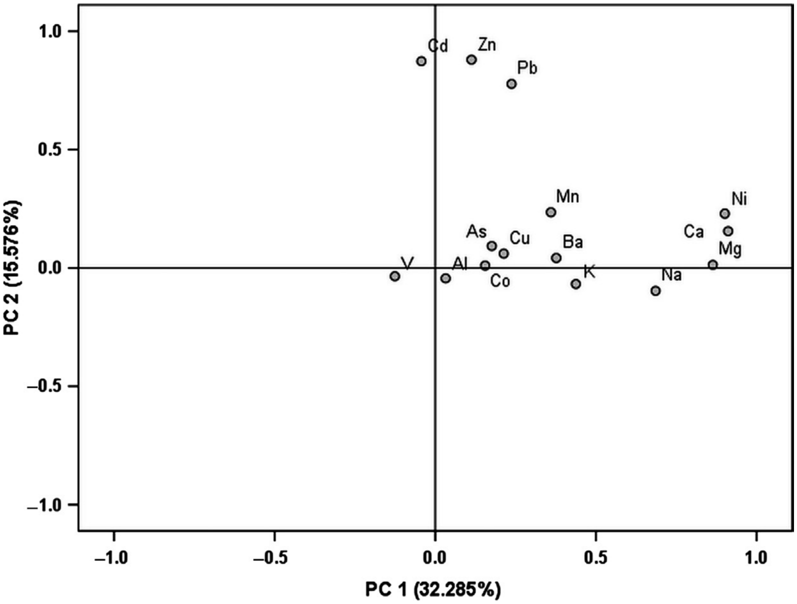

Fig. 5.3 Loading plot of analyzed minor elements.

In conclusions, the chemical quality (major constituents and trace elements) of the brands studied was variable, which possibly depends on many factors such as natural environment (geological setting, climate, topography, etc.), source water composition, and type of treatment/purification technique(s) applied during the production. The isotopic values of the Romanian bottled waters followed the same trend as LMWL, confirming the meteoric origin of these waters. The sparkling waters had higher isotopic compositions by comparison with the still waters. The Romanian mineral water could be distinguished by foreign ones only by V as parameter. PCA was able to reveal the main characteristic parameters and to split the two investigated types of waters.

The results may be useful for improving the current legislation on bottled waters, and also for guiding the consumers in the choice of different bottled water brands.

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6

EVALUATION OF WATER QUALITY AVAILABLE FOR DIRECT USE AND IN BEVERAGES IN AGRA (INDIA)

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6.1 Introduction

Water is an essential component for life on earth, which contains minerals extremely important in human nutrition (Versari et al., 2002; Brima, 2017). In a human body, nearly 70% is water. Bones, blood, and cell contain 22%, 75%, and 90% water, respectively. It is revealed in a general survey that nearly 360 million km^2 area out of 510 million km^2 is covered by sea. However, the dramatic increase in population resulted in an enormous consumption of the world's water reserves. Natural contamination of water resources mainly results from normal geological phenomena such as ore formation (Zvinowanda et al., 2008). Nevertheless, it is observed that anthropogenic activities are a major factor determining the quality of the surface and groundwater through atmospheric pollution, wastewater discharges, use of agricultural chemicals, eroded soils, and land use (Rabiet et al., 2010; Dolnicar et al., 2014).

The supply of safe potable water has a significant impact on the prevention of water transmissible diseases (Altin et al., 2009; Al-Kalbani et al., 2017). The abundance of organic compounds, toxic chemicals, radionuclides, nitrites, and nitrates in potable water may cause adverse effects on the human health (Demirak et al., 2006; Nadaraja et al., 2015). Therefore, it is essential to constantly monitor water quality used for drinking purposes (Doria et al., 2009; Gupta and Kumar, 2012; Kumar and Bahadur, 2013).

Groundwater is used as main source for domestic, irrigation, and industrial needs in India. >85% of rural and 50% of urban domestic water requirements are being met from groundwater resources, while

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irrigation accounts for around 85% of groundwater extraction (Jha, 2007; Flem et al., 2017). Water usage in India is shown in Table 6.1.

Hasty, unscientific, and unsustainable groundwater development and management in the country due to ever increasing population, urbanization, industrialization, and demands for food security is altering the hydrological and geochemical environments of the aquifers leading to deterioration of groundwater quantity and quality. Pollution of the groundwater due to geogenic and anthropogenic factors often renders the groundwater unpotable as consumption of such water can lead to various health-related complications (Sudha, 2016; Al-Barakah et al., 2017; Kovačic et al., 2017). Endemic fluorosis occurring due to consumption of groundwater polluted with fluoride is threatening the health of millions of people in India and therefore is a challenging and extensively studied national health problem (Johnson et al., 2008; UNICEF, 2008; Walia et al., 2017). High fluoride concentrations and fluorosis in the country are commonly associated with rural areas, arid and semiarid climate, granites and gneisses, and advanced stage of groundwater development (Johnson et al., 2008; Subba Rao, 2009; Gao et al., 2013; Kumar and Chaturvedi, 2014). There are many aspects of water quality to be considered for a given water sample. Some major issues are highlighted in Table 6.2.

Most of the states like Andhra Pradesh, Rajasthan, Punjab, Uttar Pradesh, West Bengal, Bihar, and Jharkhand are affected by fluoride and Arsenic. Ansa-Asare et al. (2009) has suggested that the main source of groundwater fluoride in granitic rocks is the dissolution and anion exchange with micaceous minerals and their clay products. All natural waters contain fluoride in vastly varying concentrations. Fluoride is one of the very few chemicals that have been shown to cause significant effects in people through drinking water (Akhavan et al., 2016). It is believed that low concentration of fluoride in drinking

Table 6.1 Water Use in India (Year 2011)

Sector	Percentage
Irrigation	85.33
Domestic	6.62
Industry	1.26
Energy	0.32
Other	6.47
Total	100.00

Table 6.2 Major Water Quality Issues

Common Issues of Surface and Ground Water

1. Pathogenic (bacteriological) pollution
2. Salinity
3. Toxicity (micro-pollutants and other industrial pollutants)

Surface Water	Ground Water
• Eutrophication	• Fluoride
• Oxygen depletion	• Nitrate
• Ecological health	• Arsenic
	• Iron
	• Sea water intrusion

Table 6.3 Ground Water Bodies vs Surface Water Bodies

Ground Water Source as Compared to Surface Water Source

1. They much more complex
2. Their accessibility is very much reduced as it cannot be directly reached
3. Water remains for much longer time so contamination also stays longer. In flowing water contamination may stay for few days but in deep aquifers it stay for tens of thousands of years
4. There are greater chances of interaction between water and surrounding rocks

water has beneficial effect on teeth by helping in preventing the dental caries. On the other hand, excessive amount of fluoride in drinking water or in combination with exposure to it from other sources can be detrimental to health and cause various adverse effects leading to permanent disability. These may range from minor dental fluorosis up to crippling skeletal fluorosis as the level and period of exposure increases (Aris et al., 2013). When it comes to evaluate ground water sources, they pose many problems as shown in Table 6.3.

6.2 Study Area

6.2.1 District Profile

6.2.1.1 Origin and Development

Agra is the city of the awesome Taj Mahal, one of the seven wonders of modern world. But the story of Agra city begins much earlier than the Taj. Agra is mentioned in the epic Mahabharata where it was known as Agrabana or Paradise. The famous second century geographer, Ptolemy, marked this site on his map of the world as Agra. Folklore and legends mark the current city of Raja Badal Singh (about 1475 AD) whose fort, Badalgarh, was situated on or near the site of the present fort. Also, Salman a Persian poet hailing from the 12th century AD, mentioned a huge attack on the fort of Agra, which was later held by King Jaipal and after that by Sultan Mahmud of Ghazni. But it was Mughals who later on adored Agra with the best monuments architects could imagine and put on this world to wonder. There are many such wonders spread across Agra namely Taj Mahal by Shah Jhan, Agra Fort by Akbar, Itmad-Ud-Daulah, and nearby situated Sikandra, each of which speaks in mute testimony to the city's grandeur over the ages (Agra, 2018).

6.2.1.2 Location, Boundaries, and Weather

The district of Agra lies in west UP, between 27.11′ degree Latitude North and 78.0′ degree–78.2′ degree Longitude East. Its average altitude above mean sea level is about 170 m. It is bordered by district Mathura (famous for birth place of Lord Krishna) in the north, district Firozabad (known for glasswork) lies in east, in the South side it is bordered by Dhaulpur district and in the West direction lies Bharatpur. Agra city lies on the bank of river Yamuna (Figs. 6.1 and 6.2).

In Agra, during summers maximum temperature may reach up to 48°C and minimum temperature is about 21.9°C and in winter maximum temperature in 14°C and minimum temperature is about 4°C. Most suited season for tourism is from November to March.

6.2.1.3 Area and Population

As per 1991 census, Agra district covers an area of about 4027.00 km^2. Most of it is rural area (about 3839 km^2) and out of remaining 188 km^2 is urban area. Its total population is about 27,51,021 out of which males are 15,01,927 and females are 12,49,094. Of the total population, 16,39,935 constitute the rural population and 11,11,086 makes up the urban population (Agra, 2018).

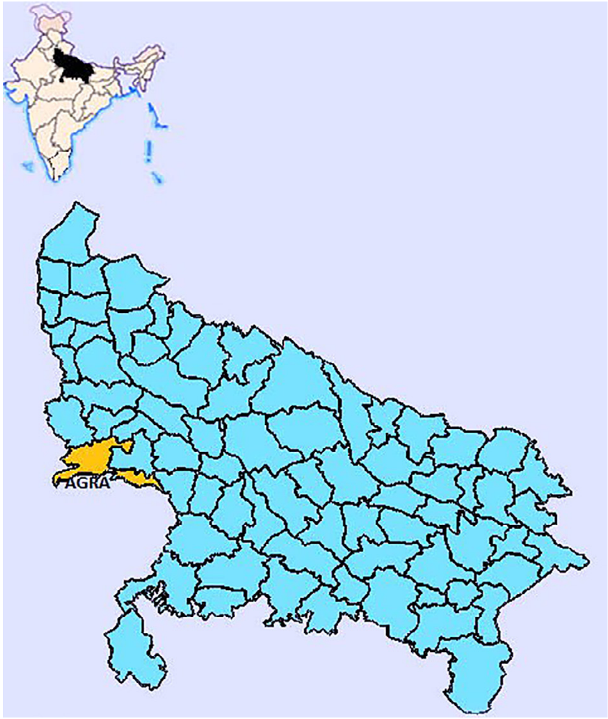


Fig. 6.1 Location map of Agra district.

Fig. 6.2 Map of Agra city.

6.2.1.4 Infrastructure

The Agra district is divided into 6 tehsils and 15 blocks. Total number of Nayay Panchayats in the district is 114 while Gram Sabhas stands at 636. The total populated villages are 904. The total number of police stations in the district is 41 out of which 16 are in urban area and 25 are in rural area. The total number of railway stations (including halts) is 29 and bus stands/bus stops are 144.

6.2.2 Economy

The economy of the Agra district is mainly agriculture based while the economy base of Agra city is small-scale industries, commerce, and trade. Main crops are wheat, paddy, bajra, mustard, potato, etc. About 40% of the total economy of Agra depends on industry (directly or indirectly). Over 7200 small-scale industrial units are spared all over the district. Agra city is famous for the leather goods, handicrafts, zari zardozi, marble, and stone carving, and inlay work. Agra is also well known for sweets (PETHA) and snacks (Dalmoth and Gajak).

6.3 Origin of the Research Problem

Since the inception, of human race, rivers, and lakes have been used as a source of drinking water. Although a normal person consumes on an average up to 4 L of water in a day but this need may vary for anyone depending mainly on climate, physical activities, and body requirements. The bottled water business is gaining momentum day by day because increasing number of water borne diseases, worsening water pollution, and increasing urbanization are leading to scarcity of clean and safe natural drinking water. Unavailability of clean drinking water at places like railway and bus stations, spots of tourist's interest, and careless attitude of various domestic agencies has pushed the growth of bottled water market upward (Chauhan et al., 2017). Water bottles of almost all the major international and national brands are available in Indian market right from the malls to railway stations, bus stations, grocery stores, and even at small corner shop. Just some years back bottle water was considered as the rich people's choice, but now it has reached even the rural areas. The growth and status of Indian Bottled Industry in comparison with Western or Asian market, India for the time being is far behind in terms of quantum, infrastructure, professionalism, and standards implementation. The per capita consumption of mineral water in India is a mere 0.5 L as compared to 111 L in Europe and 45 L in the United States. If oil is the focal point of world conflict now, it is very much possible that water may become the next bone of contention among various capitalists and even between various nations. Private beverage and water companies have been granted by the government with permits to practically control and operate our natural springs and water sources in natural parks and protected areas for water production and processing plants (gits4u, 2017).

The main sources of water in Agra include, River Yamuna, Kitham Lake, and various tube wells located in different locations in the district. Agra is situated in semiarid region therefore it faces long and hot summer season. Ground water in the area is saline and hard to very hard and River Yamuna water is also not fit for daily usage even after filtration. In view of these facts, there is a large demand for packaged drinking water round the year which goes up during summer. In order to keep cost low, local vendors also sell pouches of drinking water whose quality is doubtful. Also, the quality of packaging material is very poor. In some cases, even taste of such water is foul. No proper quality checks are performed in such manufacturing units (Fig. 6.3).

Water bottle labels provide information about composition of water. But still there is a dire need for more information for the adequate

Fig. 6.3 Photo of water pouch for sale.

assessment of water quality, so as to protect buyers and to draw guidelines for quality control and proper regulation of bottled water industry (Espejo-Herrera et al., 2013). This study becomes even more important keeping in view the large number of tourists visiting Agra and increase in consumption of packaged water recently.

Each year India consumes about 86,311 tons of technical-grade insecticides to cover 182.5 million hectare of its agricultural land. Most Indian rivers pass through these vast agricultural areas which rampantly use pesticides. This unchecked use of pesticides causes leaching of pesticides from agricultural areas to nearby water bodies. This leaching is most hazardous nonpoint—unchecked, and so, not measured correctly—source of contamination to the receiving water bodies. There is a recent study which detected the traces of perchlorate (a compound responsible for thyroid disorders) in the ground waters of south India (Nadaraja et al., 2015). Although the bottled water available in the area was free from this contamination. The nontraditional category or bulk packs (with over 5 L capacity) are growing at a fast pace, and has a current share of nearly 40%. The increasing trend of bulk water consumption in homes and institutional segments will make the way for bulk water packs to gain half of the total bottled water market within next 4–5 years; this is being seen in Agra. Packaged water today is a cottage industry in the country. Not only in the big cities, where a bottled water manufacturer can be found even in a one room establishment, in most medium and small towns and even rural areas bottled water manufacturers are mushrooming all around.

6.4 Review of Research and Development in the Subject

On gleaning through literature, we find that pollution of drinking water has received considerable attention from all quarters. Ab Razak et al. (2015) has reported environmental pollution of river and ground water due to man’s accelerated and unthoughtful activities in Malaysia catchments area. Pandey and Singh (2006) and Alsheikh (2015) studied effect of industrial wastewater on irrigation. Recently, large numbers of fish kill in the Kitham Lake was reported in local newspapers.

Declining ecosystems are having an adverse effect on human health. The existing health and morbidity pattern in urban slums are even worse than those in rural areas. Such a situation is significant in those areas where the urban environment is fast deteriorating. The eco-health of those areas calls for special attention because of socio-geographic condition.

6.4.1 River Yamuna

Approximately 57 million inhabitants are dependent on water from Yamuna. With an annual flow of nearly 10,000 $m^3$and consumption of 4400 m^3 (96% used for irrigation), the river supplies about 70% of Delhi's water requirements. Current facilities for water treatment are unable to remove the traces of pesticide from river water. Laboratories of public waterworks are not even able to detect pesticides. Worst part that Yamuna leaves Delhi in the form of a sewer, carrying with it the biological and chemical wastes of the city. In Agra, at downstream, the river water is the main source of municipal drinking water supply. Here also, the current facilities of water treatment are old and unable to cope with these toxins. Therefore, the users in Delhi and Agra intake hazardous quantities of toxic pesticide traces every time they drink water (CSE, 2007).

In Delhi, Yamuna enters at Palla village which is 15 km upstream of Wazirabad barrage. This barrage acts as a reservoir for Delhi. Delhi generates about 1900 million L per day (mld) of sewage, against an installed wastewater treatment capacity of 1270 mld. Thus, 630 mld of untreated and a large amount of partially treated sewage enter the river daily. The Wazirabad barrage releases very little water into the river. Especially during summer months, the only flow downstream of Wazirabad is of industrial and sewage effluents. Lesser discharge means lesser river flow and thus, greater levels of pollution. From the Okhla barrage, which is the exit point for the river in Delhi, from Yamuna the Agra canal branches out. During the dry months, practically no water is released from this barrage to downstream Yamuna. Instead, discharges from the Shahadara drain join the river downstream of the barrage, taking effluents from east Delhi and Noida into the river. This is the second largest polluter of the river after the Najafgarh drain.

The main problem lies in undetected and untreated pesticide residues. Waterworks officials in Delhi and Agra point out that pesticide traces cannot be removed with currently available conventional treatment. "Organic substances can be assimilated in freshwater, provided there is enough freshwater in the river," states R. Dalwani, Scientist, Ministry of Environment and Forests (MEFs). "But for micro-pollutants such as pesticides, only more freshwater can reduce the percentage of traces in water. These cannot be dissolved or assimilated, but certainly can be diluted to an extent." The river has a dilution requirement of 75%, which implies that for every 100 L of wastewater, 75 L of freshwater is required. Scientists state that with the flow of water, pollutants (especially organic pollutants) degrade to a large extent. But at every step, this purified water is abstracted, and ever larger loads of pollution make their way into the river (CSE, 2007).

Agra has spent Rs. 777.5 million on cleaning the Yamuna till September 2005; it is the second most expensive town under the Yamuna Action Plan in Uttar Pradesh. But in spite of this massive investment, the pollution loads in the river in Agra have increased by 180% from 90 mld in 1996 to 254 mld in 2005 (CSE, 2007).

The fecal coliform count, which indicates the presence of disease causing microorganisms, is nearly 25,000 times more than the limit prescribed for bathing. This was revealed at a public meeting organized by the New Delhi-based research and advocacy organization, Center for Science and Environment (CSE) here today.

"Agra and Mathura have been at the receiving end of the pollution from Delhi. The Yamuna's 22-km stretch in Delhi is barely 2% of the length of the river, but contributes over 70% of the pollution load," said S.V. Suresh Babu, Deputy Coordinator, River Pollution Campaign, CSE. In Delhi, the river has virtually no freshwater for 9 months. Delhi impounds all its water at Wazirabad, where the dammed up river practically ceases to exist; what flows subsequently is only sewage and waste from Delhi's 22 drains. There is just no water available to dilute this waste.

However, both Agra and Mathura, also contribute to the pollution in the river, their source of water. Mathura's sewerage system dates back to 1923. Although most of the investment done under Yamuna Action Plan (YAP) in Mathura was on sewerage, around Rs. 26.62 crore, the drains are in a bad state. They are silted up and incapable of transporting even dry weather flow.

The city has a treatment capacity of 28 mld and generates wastewater in the range of 49.5 mld. The rest is discharged untreated into the river. Even the treated effluent from Masani sewage treatment plant and Kulu Ka Nagla STP is discharged into the river. Hence, it is not surprising that the river remains dirty. This is despite the fact that under YAP, Rs. 2.34 crore was spent on every kilometer in the 15-km stretch of the Yamuna in the Mathura stretch (CSE, 2007).

At Agra, there are 10 drains that discharge waste upstream of the old water works at Jeoni Mandi, besides the effluent discharged from Burhi ka Nagla STP and the Peela Ghat STP. Similarly, 11 drains discharge into river downstream. The top six drains in Agra contribute over 70% of water discharge from the city.

Agra invested Rs. 777.5 million under YAP till September 2005. But the sewage discharge has increased by 180% and the biochemical oxygen demand (BOD) load has increased by 41%. "Poor planning based on suspect data has combined with faulty operations and unfulfilled maintenance promises to keep the river dirty," writers of Sewage Canal say in the book from CSE.

There is no consensus between government agencies on the amount of wastewater generated in Agra. The Central Pollution

Control Board (CPCB) puts it at 211 mld based on its figure of 210 L per capita per day of water supply. But the Uttar Pradesh Jal Nigam says that the water demand has shot up from 284 to 320 mld and hence the wastewater discharged has also increased. This difference in data affects the planning for the city.

The three STPs in Agra have a capacity to treat 35% of the domestic wastewater generated in Agra. The remaining untreated discharge goes into the river. This equation changes completely when we consider the actual amount of waste generated and treated at Agra STPs (CSE, 2007).

6.5 Interdisciplinary Relevance

The growth of industries, ever increasing human population, and misuse has led to an increased accumulation of waste materials. This process not only reduces the available fertile lands, which are used to produce food and, raw materials but also pollute water, air, and soil. To fulfill the need of nutrition to crops and protect the crops from pest and pathogen attack the synthetic chemicals and fertilizers, pesticide, herbicides, nematicides, and fungicides are used which enter the soil. Soil deterioration, increasing pollution through human, animal food, and agricultural residues are the major concern facing mankind.

The deterioration of water quality is not only national but also of international concern. It has been of great concern for, human kind and drinking water quality problem may possibly lead to the next world war.

6.6 Significance of the Study

The emphasis on increased industrial production and population growth has resulted in an increased pollution problem, which if unchecked could lead to environmental degradation and health risks. The environmental degradation and destruction are multidimensional as it damages the quality of air, water, and soil which are most essential requirements of human life.

The population of Agra is experiencing fresh water shortage. This is being aggravated by steady deterioration of water quality of the city. The most worrying factor is high concentration of heavy metals, regime pesticides, weedicides, and insecticides in water which enter human system through the food chain. The solid waste dumps directly or indirectly contribute toward pollution of water, soil and are thereby enacting health hazards.

Recently, great number of fish kills is being reported in local newspapers. This is being attributed to low or absent dissolved oxygen (DO) in water bodies.

6.7 Materials and Methods

Ten samples of bottled and five samples of pouched water were purchased from local markets. Two samples of tap water from different locations were collected in clean sterile bottles while four ground water samples were taken from bore wells from four locations in different parts of city as given in Tables 6.4 and 6.5.

6.7.1 Groundwater Sample Collection for Physicochemical Properties

Collection of water samples was done in bottles soaked in 10% HNO_3 washed three times with double distilled water rinsed several times, leaving the last rinse for 5 min to equilibrate, water samples were collected in acidified polyvinyl chloride (PVC) bottles. At the sampling sites after determining pH, water samples were acidified with concentrated HNO_3 to lower the pH of sample to below pH 2.

The samples placed in polyethylene bags and were transported immediately to the laboratory. All bottles were stored in a dark place and in their original closed plastic containers at room temperature until the fluoride and other analysis were made. After shaking the bottle of water, a 50-mL sample was taken and kept in container, then coded

Table 6.4 Ground Water Sampling Stations

S. No.	Place	Area Type	Direction	Depth (Approx) (m)
1	Lawyers Colony	Residential	N	40
2	Mehtab Baag	Garden	S	20
3	Sikandra	Residential	W-SW	40
4	Agra College	Institute	Center	30

Table 6.5 Tap Water Sampling Stations

S. No.	Place	Area Type	Direction
1	Balenganj	Residential	E
2	Wazirpura	Residential	Center

so the type and the brands were unknown by the technician testing the water. Water samples were diluted with equal quantities of total ionic strength adjustment buffer (TISAB) and the fluoride ion concentration was determined using a colorimetric method (alizarin dye). Other parameters were determined as per standard methods (APHA, 1999). Two readings were taken for each sample then the average was recorded.

6.8 Results and Discussions

The physicochemical parameters of drinking water samples from four different locations of Agra city are given in Table 6.4. Tap water sampling stations are given in Table 6.5. The results for 15 packaged water samples are given in Table 6.6. These results were compared with the World Health Organization (WHO), Indian Standards Institute (ISI), CPCB, and Indian Council of Medical Research (ICMR) drinking water standards. The variation among the different parameters can be attributed to the different sources used for water and its geological properties. The chemical composition of natural water depends on many factors like underground rocks this water comes in contact, time in contact, rainfall, climate, and topography of study area. Metabolism of aquatic ecosystem is regulated by water temperature. Higher water temperature put stress on aquatic ecosystem as it decreases the ability of water to absorb and retain essential dissolved gases like oxygen. Often fish kill reported in summers can be attributed to reduced levels of DO in water body due to higher temperature.

6.8.1 pH

This is a measure of the acidic or basic (alkaline) nature of a sample. The concentration of the hydrogen ions in any sample determines its pH. The mathematical expression for pH is given as

$$\mathrm{pH} = -\log_{10}\left(\mathrm{H}^{+}\right)$$

Although the pH of pure water is 7.0, drinking water and natural water exhibits a pH range above 7.0 because it contains dissolved minerals and gases. Usually, the natural waters are alkaline owing to the pressure of carbonates. These are generated by CO_2 absorbed from atmosphere. As we burn fossil fuels, CO_2 is generated which escapes to atmosphere. This atmospheric CO_2 is added to sea water to form carbonic acid and the pH of sea water may show a decline. Therefore, declining pH of sea water can also be taken as a strong indicator of global air pollution. Photosynthetic activity is also responsible for pH changes. In this process, CO_2 is consumed as a result pH changes. pH is also useful in fixing the alum dose in drinking water treatment.

Table 6.6 Summary of Parameters Measured in Various Water Samples From Agra

		Packaged Water			Ground and Tap Water		
S. No.	**Parameter**	***n***	**Mean ± SD**	**Min.-Max.**	***n***	**Mean ± SD**	**Min.-Max.**
1	pH	15	7.152 ± 0.52	6.12–7.9	6	7.9 ± 0.14	7.7–8.1
2	DO	15	4.77 ± 1.28	3.9–8.1	6	5.52 ± 1.63	4–8.1
3	Alkanity	15	82.53 ± 12.7	61–108	6	81.83 ± 13.9	69–109
4	EC	15	3.69 ± 2.09	1.66–9.11	6	3.46 ± 1.72	1.44–5.98
5	TDS	15	247.53 ± 136	108–587	6	756.5 ± 247.5	574–920
6	Turbidity	15	1.27 ± 0.38	0.8–2.0	6	1.86 ± 0.37	1.6–2.6
7	TH	15	331.26 ± 247.6	44–654	6	768.3 ± 277.4	480–1280
8	Chloride	15	63.86 ± 20.15	25–90	6	456.8 ± 247.2	234–850
9	Fluoride	15	1.37 ± 0.53	0.6–2.2	6	2.02 ± 0.94	0.7–3.1
10	Potassium	15	4.73 ± 1.66	2–8	6	5.33 ± 1.033	4–7
11	Sodium	15	43 ± 15.88	27–82	6	144.1 ± 13.9	129–162
12	Calcium	15	21.47 ± 3.58	18–31	6	20.33 ± 1.86	18–23
13	Phosphate	15	≈ 0.1	–	6	‹0.1	–
14	Magnesium	15	60.4 ± 16.5	40–98	6	49.83 ± 20.7	26–88
15	Sulfate	15	10.8 ± 3.49	5–18	6	29.5 ± 6.47	21–40
16	Bicarbonate	15	83.33 ± 24.1	40–150	6	109.83 ± 23.2	65–130

Therefore, pH is a very important governing factor in a number of operations in hard-water and wastewater treatment process. Water with a pH <6.5 is considered acidic. This water typically is corrosive and soft. Water with a pH higher than 8.5 is considered basic or alkaline. This water often is hard water, the pH values of water samples under study varied between 6.12 and 8.1. All of them were found within the limit prescribed by the WHO and others except one pouched sample which had pH 6.12.

6.8.2 Dissolved Oxygen

Analysis of DO measures the amount of oxygen that is dissolved in the taken sample of at a particular temperature. Oxygen is introduced in water through diffusion from the atmosphere, through aeration caused by rapid motion and also as waste product of photosynthesis. But the total dissolved gas should not exceed 110% (DO $>13\,\mathrm{mg\,L^{-1}}$). Above this level, DO concentration can be harmful to aquatic life. Although a rare occurrence but fishes in such water may suffer from "Gas bubble disease." The gas bubbles may block the blood vessels causing obstruction of blood flow and ultimately resulting in death. This disease can also affect aquatic invertebrate but at a much higher levels than that for fish.

In liquid wastes, DO is the factor that determines whether the biological changes are brought about by aerobic or by anaerobic organisms. The former use of free oxygen for oxidation of organic and inorganic matter and produce innocuous end products, whereas the latter bring about such oxidations through the reduction of certain inorganic salts such as sulfates, and the end products are often very obnoxious. Since both types of organisms are ubiquitous in nature, it is highly important that conditions favorable to the aerobic organisms (aerobic conditions) be maintained. Thus, DO measurements are vital for maintaining aerobic conditions in natural waters that receive polluting matter and in aerobic treatment process intended to purify domestic and industrial wastewater. Aquatic organisms depend on oxygen dissolved in water just like land inhabitants depend on the quantity of oxygen present in air. The oxygen present in water can be dissolved from air or is produced by photosynthetic organisms like algae and other aquatic plants. The DO reflects the physical and biological process prevailing in the water; therefore, its measurement is of prime importance. A definite level of DO is required to sustain the higher life forms in water (Table 6.7).

The oxygen balance of the system also determines the effects of wastewater discharge. Nonpolluted surface waters are normally saturated with DO. It is rapidly depleted by the discharge of oxygen demanding wastes. The inorganic reducing substance like hydrogen

Table 6.7 Relationship Between the Dissolved Oxygen (DO) of a Water Body and Productivity of Fish

DO (mg L^{-1})	%Production (Optimum)
5.0	100
4.5	90
4.0	97
3.5	40
3.0	0

sulfide, ammonia, ferrous ions, and other oxidizable substance also tend to deplete DO. Major depletion in oxygen levels indicates heavy pollution by organic matter, the main source of which is domestic sewage. In extreme case, oxygen sometimes totally disappears from water and in this situation fishes and other organisms may be killed, as they require a certain level of DO. Game fish needs at least 5 mg L^{-1} DO whereas coarse fish can survive even at 2 mg L^{-1} of DO. DO also implants freshness and taste to water.

The determination of DO indicates the nature of the process going on in water, that is, aerobic or anaerobic. It also indicates the efficiency and thus performance of wastewater treatment plants. The DO determination is a very important factor in the field of fisheries. The self-purifying capacity of water is also reduced by the low quantity of DO. From the industrial point of view, it is also important as high amount of DO can corrode the pipes and boilers and thus its removal is needed. DO values were found between 4.0 and 8.1 mg L^{-1} in the present study. The DO study of ground and tap water confirms the fact that organic pollution is mild in the study zone.

6.8.3 Total Dissolved Solids

Various types of minerals present in a dissolved state that is, true solution; constitute the total dissolved solids (TDS) in water. Apart from these, some dissolved organic matter may also contribute to TDS. This is determined using standard methods (APHA, 1999) in the residue left after evaporation of filtered sample at 103–105°C in an oven.

The higher value of dissolved solids indicates pollution in water. Various salts like sulfates, nitrates, chlorides and phosphates of sodium, calcium, magnesium, and other cations are included in TDS. This parameter increases the density of water and effects osmoregulation of fresh water organisms, reduce solubility of gases. Apart from these, some dissolved organic matter may also contribute to TDS. TDS indicate the salinity behavior of groundwater. Water containing >500 ppm of TDS is not considered desirable for drinking purpose. The concentration of dissolved solids in water gives an idea about the suitability of water for various purposes particularly in agriculture. Water containing high concentration of minerals is unsuitable for many industrial uses.

A plot of TDS vs electrical conductivity gives straight line. These curves on extrapolation pass almost through origin. This proves that electrical conductivity becomes negligible when TDS are zero. This in agreement with the fact that electrical conductivity is directly proportional to the dissolved solids present in water TDS values are found in between 108 and 920 mg L^{-1}. The highest value is shown by a tap water sample indicating higher quantity of dissolved solids.

6.8.4 Electric Conductivity

The ability of an aqueous solution to carry an electrical current is expressed in terms of a numerical expression called conductivity. This depends on the presence, mobility, valency, and concentrations of the ions. It also depends on the temperature at which observation is made. Therefore, the presence of most inorganic acids, bases, and salts increases the conductivity of water sample. On the other hand, organic compound molecules, which do not dissociate, do not contribute to conductivity. High conductivity indicates a larger quantity of dissolved minerals salts in water, thereby making it sour and unsuitable for drinking. Electrical conductivity values in this study ranges as 1.44–9.11 mS. The higher electric conductivity (EC) values are observed in ground water samples. It indicates the higher amount of total dissolved salts.

6.8.5 Turbidity

Turbid water cannot be used directly in most industries and require treatment before use. The photosynthetic activities in the river water are also affected as the penetration of sunlight is hindered. The probability of pathogenic organism's presence is more in turbid water which is also aesthetically objectionable for drinking and many other uses. The cost of water treatment goes up when the intake water becomes more turbid. Clear waters are particularly needed for manufacturing uses like beverage products, food products, drinking products, etc. The drinking water limit for turbidity is 2.5 NTU (WHO). The observed values of turbidity in the present study vary from 0.8 to 2.6 NTU only one sample (tap water sample) exceeding WHO limit. This may be attributed to some filter problem as all the samples in this study are supposed to go through filtration. The sample showing highest turbidity also shows highest TDS value.

6.8.6 Fluoride

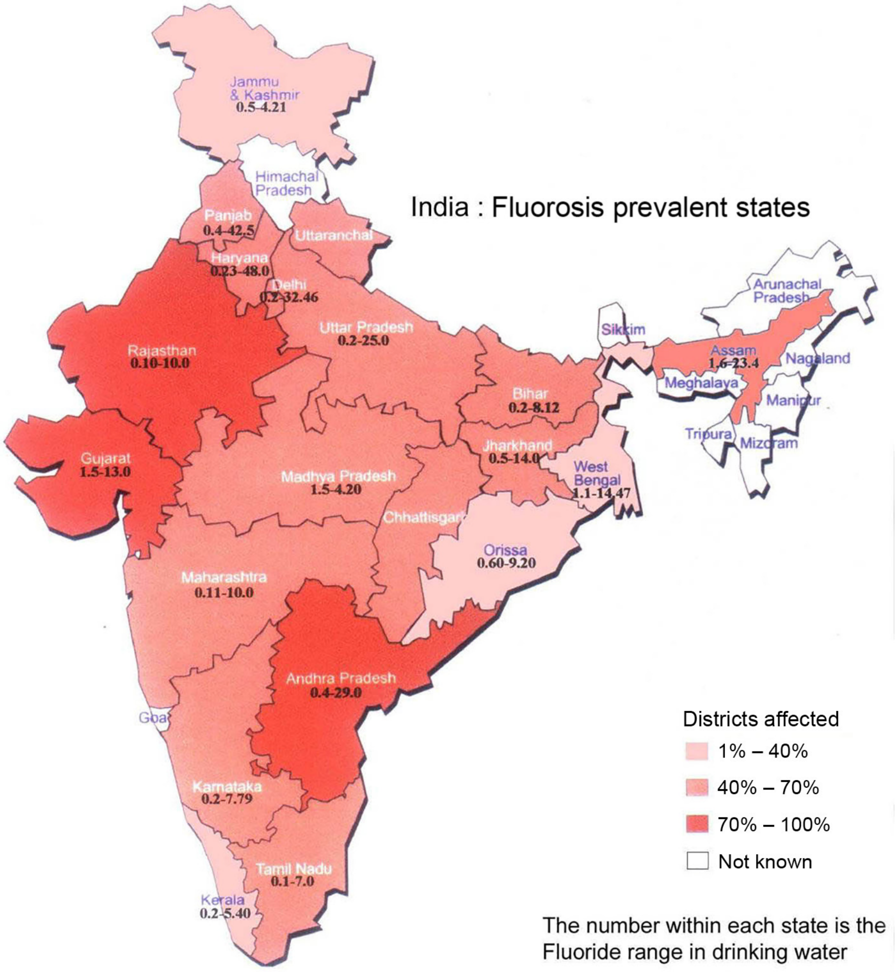
According to the WHO and Indian standards, the maximum permissible limit is 1.5 mg L^{-1}. But the highest desirable limit is 1 mg L^{-1}. Fluoride concentrations above 1.5 ppm in drinking water cause dental fluorosis and much higher concentration skeletal fluorosis. Low concentration (~0.5 ppm) provides protection against dental caries. India is among the 23 nations around the globe where health problems occur due to the consumption of fluoride contamination water and the extent of fluoride contamination in water varies from 1.0 to 400 mg L. In India, 20 million people are severely affected by fluorosis and 40 million people are exposed to risk of endemic fluorosis (Subba Rao, 2009). In India, fluoride endemic states one Andhra Pradesh, Karnataka, Tamil Nadu, Punjab, Haryana, Maharashtra, Gujarat, Rajasthan, Uttar Pradesh, Kerala, Jammu and Kashmir, and Delhi (Fig. 6.4).

Knowledge of fluoride content of drinking water is important for public and health care professionals to know. Planning of preventive dental care programs depend on the correct assessment of F intake by the people as enamel fluorosis from excessive ingestion of fluoride can lead to long-term adverse health effects. In the present study, many samples far exceed the recommended limit of fluoride. Some packaged water samples (three bottled and two pouch samples) also exceed the stipulated limit. The highest value of 3.1 mg L^{-1} was observed in ground water sample.

6.8.7 Hardness

Hard water is not suitable for washing purpose, as the lather formation with soap is hindered by the hardness. It also increases the boiling point of water. Principal cations responsible for hardness of water are calcium and magnesium. Apart from these ions strontium, iron and manganese also contribute to it. The anions responsible for hardness are mainly bicarbonates, carbonates, sulfates, chlorides, nitrates, etc. Although hard water has no known ill effects on health but it is unsuitable for domestic uses. It also forms heat insulating scales in the boilers and other heat exchange equipments, reducing their efficiency. Therefore, hard water is unsuitable for industrial purpose also. The maximum allowable limit of total hardness is 500 mg L and the most desirable limit is 100 mg L^{-1} as per the WHO standards (Table 6.8).

But the hardness is useful in certain conditions. In the public water supply, it prevents the corrosion in the lead pipe by forming a thin layer of scale and reduces the entry of lead from the pipe into the water. Drinking water supplies with total hardness below 250 ppm is considered acceptable. Groundwater of all stations exceeds limit of hardness as permitted by ISI (Table 6.9).



Source of information: (1) UNICEF State of Art Report, 1999
(2) FR & RDF data bank

Fig. 6.4 Fluoride map of India.

Large numbers of graphical and statistical methods are available to depict the relative concentrations of various ionic components of natural water. One of the most used methods is Piper diagram (Piper, 1944). It graphically shows the relative abundance or occurrence of ionic constituents in a given water sample. In this diagram, %meq L^{-1} of four main cations (sodium, potassium, magnesium, and calcium) are plotted in cation triangle. Similarly, %meq L^{-1} of main anions (chloride, sulfate, and bicarbonate + carbonate) are plotted in anion triangle. The data points on the two triangles (cation and anion) are

Table 6.8 Classification of Water Bodies According to the Hardness

Hardness (ppm)	Water Quality
0–60	Soft
61–120	Moderately hard
121–180	Hard
>180	Very hard

Table 6.9 Classification of Water Samples on the Basis of Hardness

Sample No.	Hardness	Quality on the Basis of Hardness
1	89	Moderately hard
2	25	Soft
3	83	Moderately hard
4	79	Moderately hard
5	39	Soft
6	73	Moderately hard
7	60	Soft
8	68	Moderately hard
9	42	Soft
10	83	Moderately hard
11P	90	Moderately hard
12P	70	Moderately hard
13P	62	Moderately hard
14P	55	Soft
15P	40	Soft
16G	234	Very hard
17G	673	Very hard
18G	283	Very hard
19G	850	Very hard
20T	319	Very hard
21T	382	Very hard

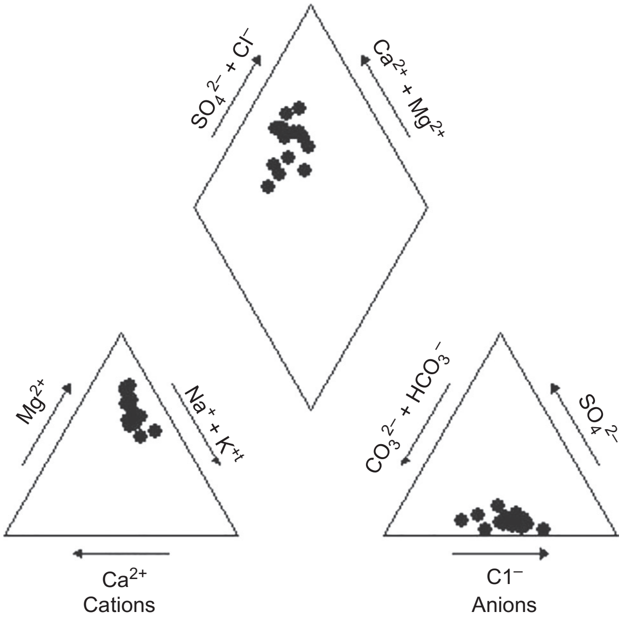


Fig. 6.5 Piper diagram.

then combined in the quadrilateral box which gives the overall chemical composition of water sample in question (Fig. 6.5).

As seen from Piper diagram in figure, the most abundant type is Na-K-Cl. But the detailed information is not obtained from water type. In the present study, hardness values range between 80 $\mathrm{mg\,L^{-1}}$ (bottled water) and 1608 $\mathrm{mg\,L^{-1}}$ (ground water). Usually, ground water in Agra is very hard. On standing ground water leaves white crust on utensils. This water is unsuitable for watering plants. Fig. 6.6 shows white crust in a flower pot.

6.8.8 Alkalinity

The alkalinity of a water sample is its quantitative capacity to neutralize a strong acid to a designated pH (APHA, 1999). It is significant for many uses and treatment of natural and wastewater. The alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide contents. Its value is taken as an indication of the concentration of these constituents. The alkalinity is significant in determining the suitability of water for irrigation. Raw domestic wastewater has an alkalinity only slightly greater than that of the water supply. For industrial wastes, the measurement can indicate change in quality. Its values ranged between 61 and 109 $\mathrm{mg\,L^{-1}}$ for all samples which is well below recommended level as given by the CPCB.

Fig. 6.6 Photo of flower pot.

6.8.9 Na

Sodium ranks sixth among the elements in order of abundance and is present in natural waters. The levels may vary from negligible to appreciable. Relatively high concentrations may be found in hard water softened by the Na-exchange process. The ratio of sodium to total cations is important in agriculture and human pathology. Soil permeability is harmed by high sodium ratio. A limiting concentration, of 2–3 mg L^{-1} is recommended in feed waters for high-pressure boilers. It was present in larger quantities as compared to potassium. Minimum value was 27 mg L^{-1} (packaged water) and maximum was 162 mg L^{-1}. All the ground water and tap water had higher amount of sodium this may explain salty taste of these water samples.

6.8.10 Potassium

Potassium is an essential element in humans and is seldom, if ever, found in drinking water at levels that could be a concern for healthy humans. The recommended daily requirement is >3000 mg. Potassium occurs widely in the environment, including all natural waters. It can also occur in drinking water as a consequence of the use of potassium permanganate as an oxidant in water treatment. In some countries, potassium chloride is being used in ion exchange for household water softening in place of, or mixed with, sodium chloride, so potassium ions would exchange with calcium and magnesium ions. Possible replacement or partial replacement of sodium salts with potassium salts for conditioning desalinated water has been suggested. Currently, there is no evidence that potassium levels in municipally treated drinking water, even water treated with potassium permanganate, are likely to pose any risk for the health of consumers. It is not considered necessary to establish a health-based guideline value for potassium in drinking water (WHO).

Although potassium may cause some health effects in susceptible individuals, potassium intake from drinking water is well below the level at which adverse health effects may occur. Health concerns would be related to the consumption of drinking water treated by potassium-based water treatment (principally potassium chloride for regeneration of ion exchange water softeners), affecting only individuals in high-risk groups (i.e., individuals with kidney dysfunction or other diseases, such as heart disease, coronary artery disease, hypertension, diabetes, adrenal insufficiency, preexisting hyperkalaemia; people taking medications that interfere with normal potassium-dependent functions in the body; and older individuals or infants. It is recommended that susceptible individuals seek medical advice to determine whether they should avoid the consumption of water (for drinking or cooking) treated by water softeners using potassium chloride (WHO). In the present study, variable amount (2.0–8.0 $\mathrm{mg\,L^{-1}}$) of potassium was found in different water samples.

6.8.11 Calcium

The natural presence of calcium in winter results from passage over deposits of limestone, dolomite, gypsum, and gypsiferous shale. The course of Yamuna runs through area of shale and lime stone sequence of Krol series. Apart from this, a number of industries dump their polluted wastes in the river. The acidity of water used for industrial purpose is controlled by the use of lime. Calcium is largely responsible for the hardness of water, which in turn reduces the utility of water for domestic and industrial purposes. Calcium values ranged from 18 to 31 $\mathrm{mg\,L^{-1}}$. Most of higher values shown by packaged water samples.

6.8.12 Phosphate

Phosphorus is one of the essential elements necessary for growth of plants and animals. Phosphorus in its elemental form is very toxic and is bioaccumulated in body. Phosphate PO_4^{3-} contains this element. Phosphate mainly exists in three forms: orthophosphate, metaphosphate, and organically bound phosphate. Each of these compounds contains phosphorus in a different chemical statefvortho forms are produced by natural processes and are found in sewage. Poly forms are used for treating boiler water and in detergents. In water, they change into the ortho form. Organic phosphates are important in nature. Their occurrence may result from the breakdown of organic pesticides which contain phosphates. They may exist in solution, as particles, loose fragments, or in the bodies of aquatic organisms.

Rainfall can wash varying amounts of phosphates from farm soils into nearby water bodies. Phosphate can promote the growth of plankton and aquatic plants which provide food for fish. This increase in growth may cause an increase in the fish population and hence improve the overall water quality. However, if an excess of phosphate enters the water way, algal and aquatic plants will grow uncontrollably, they can choke up the water way, and use up large amounts of DO. This condition is called eutrophication or over fertilization of receiving waters bodies. The rapid growth of aquatic vegetation can cause the death and decay of vegetation- and quality life becomes poor due to the fall in DO levels. Phosphates are nontoxic to people or animals until and unless their levels are very high. Very high levels of phosphate can cause digestive problems.

The inorganic compounds of phosphorus of significance in environmental practice are phosphate or their molecularly dehydrated forms (polyphosphate). Organically bound phosphorus is of minor consideration. All surface water supplies support growth of minute aquatic organisms. The free swimming and floating organisms are called plankton. These are composed of animals (zooplankton) and plants (phytoplankton). The latter are predominantly algae and cyanobacteria, and since they are chlorophyll-bearing organisms, their growth is influenced greatly by the amount of fertilizing elements in the water. Nitrogen and phosphorus are both essential for the growth of algae and cyanobacteria and that limitation in amounts of these elements is usually the factor that controls their rate of growth. Where both nitrogen and phosphorus are plentiful, algal blooms occur which may produce a variety of nuisance conditions. Phosphates hold a very important position among fertilizers and are important ingredient of fertile soil. They are extensively used in the agricultural activities. The main source of phosphate in river or ground water is the agricultural runoff. The other sources include domestic waste, decaying organic matter, and naturally occurring phosphate minerals. Domestic wastewater is relatively rich in phosphorus compounds. Prior to the development of synthetic detergents, most of the inorganic phosphorus was contributed by human wastes as a result of the metabolic breakdown of proteins and elimination of the liberated phosphates in the urine.

Most heavy-duty synthetic detergent formulas designed for the household market contain large amount of polyphosphates as "builders." The use of these materials as a substitute for soap has greatly increased the phosphorus content of domestic wastewater. In the present study, the levels of phosphate in all samples are well below harmful level. Phosphate levels were mostly below 0.1 $\mathrm{mg\,L^{-1}}$ in most of the samples.

6.8.13 Chloride

The most common inorganic anion present in water and wastewaters is chloride in the form Cl^- ion. Chlorides are the inorganic compound resulting from the combination of the chlorine gas with metal. Some common chlorides include sodium chloride (NaCl) and magnesium chloride (MgCl). Chlorine alone as (Cl) is highly toxic, and it is often used a disinfectant (Kumar and Puri, 2012). In combination with a metal such as sodium, it becomes essential for life. Small amounts of chlorides are required for normal cell functions in plant and animal life. Environmental impacts of chlorides are not usually harmful to human health; however, the sodium part of the table salt has been linked to heart and kidney diseases. The salty taste in potable water caused by chloride concentration is variable and dependent on the chemical composition of the water, mainly the cations. Some waters containing 250 mg L^{-1} chlorides may have a detectable salty taste in the presence of sodium cation. On the other hand, waters, containing 1000 mg L^{-1} chloride may not have a salty taste in presence of calcium and magnesium cations. The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system. Its concentration may also be increased by industrial activity. Although it occurs naturally in all types of waters, but the important source is domestic sewage. Man and animals excrete, along with nitrogenous compounds, high quantities of chlorides. Therefore, its concentration is used as an indicator of sewage contamination. Before the development of bacteriological and other tests like BOD and chemical oxygen demand (COD), chloride concentration was used as a parameter to indicate sewage contamination.

Chlorides are highly soluble with most of the naturally occurring cations and do not precipitate and cannot be removed biologically in treatment of wastewater. In many areas, the level of chlorides in natural waters is an important consideration in the selection of supplies for human, industrial, and agricultural use. Where brackish waters must be used for domestic purpose, the amount of chlorides present is an important factor in determining the type of desalting apparatus to be used. The chloride determination is used to control pumping of groundwater from locations where intrusion of seawater is a problem (Sawyer et al., 2010). In area where the discharge of salt-water brines and industrial wastes containing high concentration of chlorides must be controlled to safeguard receiving waters, the chloride determination serves to excellent advantage for regulatory purpose.

Chloride values in present study ranged from 25 to 850 mg L^{-1}. Ground water sample had highest concentration of chloride 850 mg L.

So far no adverse effects have been observed on human beings regularly consuming water with much higher concentrations of chloride.

6.8.14 Magnesium

Magnesium ranks eighth among the elements in order of abundance and is a common constituent of natural water. Magnesium is an important contributor to the hardness of water, magnesium salts break down on heating to form scale in boiler. It is also an important constituent of chlorophyll and in small amount, it is required for photosynthesis. But when it is present in larger concentration, it reduces the utility of water for domestic and industrial uses by increasing the hardness. Magnesium values ranged from 26 to 98 $\mathrm{mg\,L^{-1}}$. Packaged water samples had relatively higher values as compared to other water samples.

6.8.15 Bicarbonate

Bicarbonate is a major element in our body. Secreted by the stomach, it is necessary for digestion. When ingested, for example, with mineral water, it helps to buffer lactic acid generated during exercise and also reduces the acidity of dietary components. Finally, it has a prevention effect on dental cavities. In the sea water and most fresh water bodies dissolved inorganic carbon mainly exists in the form of bicarbonate. In the carbon cycle of nature it forms an important part in the form of sink. In freshwater environment, during daytime in presence of sunlight, freshwater plant undergoes strong photosynthetic activity and in the process gaseous oxygen is released and bicarbonate ions are also produced. Due to this process, the pH increases and in some cases, the degree of alkalinity may become toxic for some organisms. Apart from that, this pH increase can make other chemical compound like ammonia toxic. In the absence of light during night photosynthesis stops, now in respiration process carbon dioxide is released and production of new bicarbonate ions is stopped, this results in quick decrease in pH. But in higher quantity, it is hazardous for irrigation. Bicarbonate and carbonate ions combined with calcium or magnesium will precipitate as calcium carbonate ($CaCO_3$) or magnesium carbonate ($MgCO_3$) when the soil solution concentrates in drying conditions. The concentration of Ca and Mg decreases relative to sodium and the sodium adsorption ratio (SAR) index will be bigger. This will cause an alkalizing effect and increase the pH. Therefore, when a water analysis indicates higher pH level, it may be a sign of a high content of carbonate and bicarbonates ions. Bicarbonate levels above 210 $\mathrm{mg\,L^{-1}}$ can cause deposition of lime on the leaves. In the current highest observed value is 150 $\mathrm{mg\,L^{-1}}$ that is well below dangerous level.

6.8.16 Sulfate

Sulfate is widely distributed in nature and may be present in natural waters in varying concentrations. Sodium and magnesium sulfate exert a cathartic action and should not be present in excess in drinking water (APHA, 1999). Sulfates are important in both public and industrial water supplies because of the tendency of waters containing appreciable amounts to forms hard scales in boilers and heat exchangers.

Sulfates are of considerable concern because they are indirectly responsible for two serious problems often associated with the handling and treatment of wastewaters. These are odor and sewer-corrosion problems resulting from the reduction of sulfates to hydrogen sulfide under anaerobic conditions, as shown in the following equations (Sawyer et al., 2010):

$$SO_4^{--} + \text{Organic matter} \xrightarrow{\text{anaerobic bacteria}} S^{--} + H_2O + CO_2$$

$$S^{--} + H^+ \Leftrightarrow HS^-$$

$$HS^- + H^+ \Leftrightarrow H_2S$$

6.8.16.1 Odor Problems

In the absence of DO and nitrates, sulfates serve as a source of oxygen (or more correctly as an electron acceptor) for biochemical oxidations produced by anaerobic bacteria. Under anaerobic conditions, the sulfate ion is reduced to sulfide ion, establishes equilibrium with hydrogen ion to form hydrogen sulfide. At pH levels below 8, the equilibrium of reaction changes quickly toward the formation of unionized H_2S and is about 80% complete at pH 7. Under such conditions, the partial pressure of hydrogen sulfide becomes great enough to cause serious odor problems whenever sulfate reduction yields a significant amount of sulfide ion. Concentrations in air above 20 ppm should be avoided because of toxicity.

6.8.16.2 Corrosion of Sewers

Bacteria capable of oxidizing hydrogen sulfide to sulfuric acid is ubiquitous in nature and is always present in domestic wastewater. It is natural that some of these organisms should infect the walls and crown of sewers at times of high flows or in some other manner. Because of the aerobic conditions normally prevailing in sewers above the wastewater, these bacteria oxidize the hydrogen sulfide to sulfuric acid:

$$H_2S + 2O_2 \xrightarrow{\text{bacteria}} H_2SO_4$$

And the latter, being a strong acid, attacks the concrete. Bacteria of the genus *Thiobacillus* are capable of sulfide oxidation to sulfuric acid at pH as low as 2 (Sawyer et al., 2010). In the present study, its value ranged from 5 to 40 $\mathrm{mg\,L^{-1}}$. Lowest value shown by bottled sample while highest value by tap water sample.

6.9 Conclusion

The quality of water for human consumption has always been and still is one of the most serious challenges. There is a large variation in the water composition of different brands. The ground water contains excess fluoride with high to very high hardness in almost all locations of the city. Large population is dependent on groundwater for domestic and irrigation activities, which is not suitable for use. The longer usage of such polluted water may cause serious health disorders among people. Therefore, it is not advisable to use it directly for drinking or use in beverages without proper treatment. The tap water supply also has excess fluoride contents. Bottled drinking water available in Agra contained variable concentrations of fluoride, but mostly they were in safe zone so as not to cause any adverse effects. Also, none of the products displayed the fluoride concentration on the label. Thus, it is suggested that the bodies governing the water quality should set stringent laws regulating the mineral content of the water, both bottled and marketed. There is also an urgent need to educate masses about the proper handling of plastic water bottles as phthalates may leach in drinking water from polyethylene terephthalate (PET) bottles. Although this problem is not substantial at low temperatures and freezing conditions (Jeddi et al., 2015). It was also found during this study that children are more inclined toward sugar beverages as compared to plain water. Therefore, there is a need to promote the consumption of plain water as the beverage of choice to meet the daily hydration needs. Healthy food and beverage patterns, developed during childhood, are an integral component of a healthy lifestyle (Vieux et al., 2017).

During this study another problem came across when it was found that the limits for all the relevant parameters are not properly defined by various agencies like the United States Environmental Protection Agency (USEPA), WHO, ISI, ICMR, and CPCB as shown in Table 6.10 (Kumar and Puri, 2012). The norms lay down by these agencies act as the basis for deciding quality of a particular water sample by various public health officers and researchers. But there are discrepancies among the prescribed permissible limits of drinking water put forward by these agencies. The permissible limits of various parameters as given by different agencies show ambiguity. Turbidity (NTU): is given as 10 NTU by the ISI, 25 NTU by the ICMR, 10 NTU by the CPCB, pH

Table 6.10 List of Parameter Limits (Kumar and Puri, 2012)

S.-No.	Parameter	USEPA	WHO	ISI	ICMR	CPCB
1	pH	6.5–8.5	6.5–8.5	6.5–8.5	6.5–9.2	6.5–8.5
2	Turbidity NTU	–	2.5	10	25	10
3	Conductivity (mS)	–	–	–	–	2000
4	Alkalinity	–	–	–	–	600
5	Hardness	–	500	300	600	600
6	Chloride	250	200	250	1000	1000
7	Calcium	–	75	75	200	200
8	Magnesium	–	50	30	–	100
9	Fluoride	1.5	1.5	0.6–1.2	1.5	1.5

is unanimously agreed between 6.8 and 9.2. Total hardness also shows some variation (ISI 300 mg L^{-1} to CPCB 600 mg L^{-1}). Chlorides show wide difference USEPA 250 mg L^{-1}, WHO 200 mg L^{-1}, ISI 250 mg L^{-1}, and ICMR and CPCB 1000 mg L^{-1}. Sulfate an important parameter depicting trophic status of water quality is not defined by the USEPA and WHO but the ISI sets it at 150 mg L^{-1} and ICMR and CPCB 400 mg L^{-1}. For fluoride usually 1.5 mg L^{-1} is taken as upper limit but for tropical and hot countries like India lower limits are more logical as larger amount of water is required in these countries.

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7

CHEMICAL SENSORS FOR WATER POTABILITY ASSESSMENT

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7.1 Introduction

Water is one of the most essential natural resources of humanity, and the sustenance of safe supply of water intended for human consumption is a worldwide challenge of extreme importance (UNESCO, 2012). Appropriate water resource management, maintenance and protection of supplies, opportune quality control, and sanitation are the main actions for widening the access to safe drinking water to everyone (Schmidt, 2003).

The legislative basis governing water quality requirements in EU Member states is implemented by EU Water Framework Directive (The European Parliament and The Council of The European Union, 2000). Worldwide, the guidelines on the quality of drinking water are issued by the World Health Organization (WHO) (WHO, 2011). According to the WHO recommendations, the recurrent controls of several pollutants and indicators in drinking water is suggested; among them 25 parameters, such as the content of arsenic, antimony, various pesticides, bacteria, and several heavy metals, are extremely important from the health point of view, Table 7.1. The importance of these controls is evident, both to activate prompt interventions in case of anomalous revelations, and for a comprehensive approach to water quality study and forecasts of the impact of environmental contaminations and or anthropogenic pollution. Polluted waters must be considered both for health risks and for environmental problems associated with environmental contamination and receptive water bodies. Continuous collection of historical analytical series for the parameters of interest enables the assessment of data libraries necessary for the development

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Table 7.1 Parameters to Monitor in Drinking Water According to World Health Organization (WHO, 2011)

Chemical	Unit	Guideline Value	Guideline Type	Source
2,4-D	mg/L	0.03	Health	Agriculture
Aldicarb	mg/L	0.01	Health	Agriculture
Aldrin and dieldrin	mg/L	0.00003	Health	Agriculture
Aluminum	mg/L	0.1	Acceptability	
Ammonia	mg/L	1.5	Acceptability	
Antimony	mg/L	0.02	Health	Treatment
Arsenic	mg/L	0.01	Health	Natural
Atrazine	mg/L	0.002	Health	Agriculture
Barium	mg/L	0.7	Health	Natural
Benzene	mg/L	0.01	Health	Industrial, human
Boron	mg/L	0.5	Health	Natural
Cadmium	mg/L	0.003	Health	Industrial, human
Chloride	mg/L	250	Acceptability	
Chromium	mg/L	0.05	Health	Natural
Copper	mg/L	2	Health	Treatment
Cyanide	mg/L	0.07	Health	Industrial, human
DDT and metabolites	mg/L	0.001	Health	Pesticides for public health
Endrin	mg/L	0.0006	Health	Agriculture
Fecal coliform bacteria	Counts/100 mL	0	Health	
Fluoride	mg/L	1.5	Health	Natural
Hardness	mg/L	200	Acceptability	
Hydrogen sulfide	mg/L	0.05	Acceptability	
Iron	mg/L	0.3	Acceptability	
Lead	mg/L	0.01	Health	Treatment
Lindane	mg/L	0.002	Health	Agriculture
Manganese	mg/L	0.4	Health	Natural
Mercury	mg/L	0.001	Health	Industrial, human
Nickel	mg/L	0.02	Health	Treatment
Nitrate	mg/L	50	Health	Agriculture

Table 7.1 Parameters to Monitor in Drinking Water According to World Health Organization (WHO, 2011)—cont'd

Chemical	Unit	Guideline Value	Guideline Type	Source
Nitrite	mg/L	3	Health	Agriculture
pH minimum	mg/L	6.5	Acceptability	
pH maximum	mg/L	8	Acceptability	
Selenium	mg/L	0.01	Health	Natural
Sodium	mg/L	200	Acceptability	
Sulfate		250	Acceptability	
Total dissolved solids	mg/L	600	Acceptability	
Turbidity	NTU	5	Acceptability	
Zinc	mg/L	3	Acceptability	

of global models on the quality dynamics of water intended for human use in particular territories.

In Europe, the parameters to be controlled in water intended for human consumption are determined by Council Directive 98/83/EC of November 3, 1998 (http://data.europa.eu/eli/dir/1998/83/oj) and subsequent amendments in Commission Directive (EU) 2015/1787 of October 6, 2015 (http://data.europa.eu/eli/dir/1998/83/2015-10-27). A total of 48 microbiological, chemical, and physical parameters must be monitored and regularly tested. In general, WHO guidelines for drinking water and the opinion of the Commission's Scientific Advisory Committee are used as the scientific basis for the quality standards in the drinkable water (http://ec.europa.eu/environment/water/water-drink/legislation_en.html). Five major categories of pollutants have been identified; they are heavy metals, pesticides, hydrocarbons, halogenated hydrocarbons, and alkyl phenols (Díaz-González et al., 2016). Another important aspect to be considered for water intended for human consumption is its potential toxicity associated with the microbial risks elicited by the presence of bacteria (often arising from human and animal feces) and their metabolic (for instance, toxins of blue-green algae) (WHO, 2011). Table 7.2 compares the acceptable limits in drinkable water of some pollutant markers in accordance with international (WHO), European (EU), United States (USEPA), and Australia laws. It is to note that the EU guidelines are the

Table 7.2 Comparison of the Acceptable Limits in the Potable Water of Some Pollutant Markers According to WHO, EU, USEPA, and Australia

Parameter	WHO	EU	USEPA	Australia
Ammonia	1.5 mg/L	0.5 mg/L	No GL	0.5 mg/L
pH	6.5–8	No GL	6.5–8.5	6.5–8.5
Chloride	250 mg/L	250 mg/L	250 mg/L	250 mg/L
Iron	0.3 mg/L	0.3 mg/L	0.3 mg/L	0.3 mg/L
Lead	0.01 mg/L	0.01 mg/L	0.015 mg/L	0.01 mg/L
Arsenic	0.01 mg/L	0.01 mg/L	0.01 mg/L	0.007 mg/L
Copper	2 mg/L	2 mg/L	1.3 mg/L	2 mg/L
Fecal coliform bacteria	0 counts/100 mL	0 counts/100 mL	0 counts/100 mL	No GL

GL, guideline value.

more restrictive in terms of allowed concentrations with the remarkable exception of copper ions.

The analytical methodologies used in the quantitative analysis of water include the application of various chemical, physical, biological, and microbiological methods (https://www.epa.gov/dwanalyticalmethods). The proper application of many of these methods requires the facilities of specialized laboratories, equipped with the sophisticated and expensive instrumentation (e.g., spectrophotometers, mass spectrometers, equipment for various types of chromatography, etc.). Complementary requirements include the commitment of qualified operators, the large-scale use of glassware and chemical reagents (which may be a further source of pollution); the use of specialized teams for sampling, data processing, logistics, etc. Since the variable quality of water intended for human consumption has an economic cost for a community and influences its potential for use, new and more effective methods of measuring and controlling contamination must be considered, which are able to give signals of alarms in real time over the contamination event, allowing prompt remediation procedures to the event, preventing and eliminating related risks.

Of course, the continuous monitoring of potable water quality requires huge and continuous efforts to perform the measurement of all recommended parameters, or even only the mandatory ones. Nevertheless, in several works it was demonstrated that the number of pollution markers can be often reduced, while performing network water quality routine checks by standard analytical methods in combination with chemometric methods and statistical approach (Beamonte et al., 2007; Smeti et al., 2009). For example, a group of Spanish researchers compared the quality of surface water intended for human consumption in the area near Valencia, Spain, by measuring the mandatory parameters determined by EU Council Directive 75/440/EEC (the former Council Directive of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States) (Beamonte et al., 2007). Small variations in some parameters, such as temperature, sulfate content, chloride, and manganese ions, have been detected for the two main aqueducts present in the territory. Although these variations did not exceed the limits set by the law, the authors stressed the need for more frequent controls to ensure adequate consumer safety. A multivariate method based on various chemometric techniques, such as principal component analysis (PCA), discriminant analysis (DA), and regression methods, has been applied to compare the quality and efficacy of water for human consumption from the three different drinking stations located in the area around the city of Athens, Greece (Smeti et al., 2009). For the assessment of water quality, a historical analytical series was constructed, collecting, three times a month in the period of 1 year (2007), the values of the following parameters: electrical conductivity, alkalinity, pH, hardness, chloride, calcium, magnesium ion, and residual disinfectant (chlorine) concentrations. The possibility of distinguishing the waters from different potable water plants has been demonstrated. The model can be used to check the operation of drinking water stations.

Another possibility to assess the quality of drinking and surface water, as recommended by the United Nations Environment Program (UNEP) in 2005, is to calculate the Water Quality Index (WQI)—“Water Quality Index” (UNEP, 2007). WQI is a numeric value, ranging from 1 to 100, estimated on the measurement of nine major markers such as pH, dissolved oxygen (DO), total suspended solids content, turbidity, fecal coliforms, biological oxygen demand (BOD5), total amount of nitrates, and phosphates. However, there is no a general consensus about the WQI formulation. In many countries WQI is often evaluated to estimate potable water quality (Akkoyunlu and Akiner, 2012; Lumb et al., 2006; Pesce and Wunderlin, 2000; Liou et al., 2006; He et al., 2012). For instance, in Akkoyunlu and Akiner (2012) it has been shown that a minimum number of parameters, including temperature, pH, DO, total suspended solids content, and conductivity, is sufficient for the preliminary assessment of surface water quality in the area of Lake Sapanca, Turkey. The WQIeut index was suggested for the evaluation of water eutrophication; it consists of DO, orthophosphates, nitrates, nitrites, BOD5, and chemical oxygen demand (COD). The minimum index, consisting of only three parameters, DO, turbidity, and conductivity was introduced in Pesce and Wunderlin (2000) to assess the water quality of the Suguia River, Argentina. The index made from six parameters (DH—quantity of hydrolyzed proteins, COD, BOD5, DO, nitrite amounts, and hexavalent chromium) and based on statistical analysis was applied in He et al. (2012) for the evaluation of the quality of the water from the Eltrix River, Xin Jiang Province, China.

The use of chemical sensors is one of the most promising opportunities to carry out inexpensive and real-time monitoring of water quality (Buffle and Horvai, 2000). Previously a plenty of chemical sensors has been developed for the analysis of heavy metals, organic pollutants, bacteria and their metabolites, etc. Moreover, in the last few decades analytical systems mimic the natural senses, often called "Electronic tongues" or (E-tongues) due to the analogy with human taste, became more and more popular and were shown to solve a wide range of tasks, from potable water quality assessment and possible risks detection (Winquist et al., 2011; Vagin et al., 2016; Oliveira et al., 2013; Kirsanov et al., 2014) to analysis of foodstuffs (Lvova, 2016; Cetó et al., 2016) and agricultural applications (Lvova and Nadporozhskaya, 2017). Such systems are composed by a number "of semi-selective sensors with overlapping specificities and with differentiated responses towards different analytes of complex samples, accompanied with signal-processing and pattern recognition which enables a rational decision" (Vagin et al., 2016).

In this chapter, we will focus on selected applications of chemical sensors and sensor arrays for potable water analysis. The structure of this chapter is as follows: first we will describe the working principles and the main types of sensors employed in potable water quality assessment, than the ideas behind multisensor analysis exploitation, and a critical outlook on the multisensory approach in comparison to single selective sensors in natural samples will be given; we will finish this chapter with three detailed case studies devoted to the use of potentiometric, optical, and multitransduction sensor arrays, as analytical "alarm-like" systems for the toxicity assessment of water intended for human consumption in terms of algal toxins, several herbicides and pesticides, transition and heavy metals, respectively.

7.2 Classification of Chemical Sensors for Water Analysis

Chemical sensors can be mainly classified into electrochemical, gravimetric, and optical according to their transduction mechanisms (Göpel et al., 1989). In the next sections the brief overview on the main types of sensors recently applied in the literature for drinkable water quality monitoring and their working principles are described.

7.2.1 Electrochemical Sensors

The output of electrochemical sensors relies on the flow of the charge carriers (electrons) between the sensor surface and the analyte. Electrochemical sensors can be generally divided in amperometric/voltammetric? (where the current variation is measured upon analyte concentration change at fixed or varied working electrode potential), potentiometric (the electrode potential is measured versus reference electrode at zero-current conditions of external electrical circuit), coulometric (measuring the amount of electricity in coulombs consumed or produced during electrolysis), conductometric (relating the conductance according to Kohlrausch's law to the electrolyte concentration), or electrogravimetry (translate the analyte mass change the transducer resonant frequency variation).

Two main popular classes of electrochemical sensors employed in drinking water analysis are potentiometric and amperometric/voltammetric (Díaz-González et al., 2016). These sensors are highly sensitive and selective toward electroactive species, portable, not expensive; furthermore, they provide fast and accurate responses. Among them, the differential pulse and stripping voltammetry on different working electrodes were employed for the detection of heavy metals, such as lead (Li et al., 2015; Seenivasan et al., 2015; Dai and Liu, 2017), aluminum (Jun Lee et al., 2015), arsenic (Mall et al., 2014; Mukherjee et al., 2014), cadmium (Velmurugan and Chen, 2017), and mercury (Bessbousse et al., 2014; Lu et al., 2016) in particular. The detection of different organic compounds, such as pharmaceuticals (Nagaraj et al., 2014), detergent residues (Bratov et al., 2013), halogenated hydrocarbons (Garada et al., 2014), pesticides and herbicides (Fu et al., 2015; Rahemi et al., 2015; Qian et al., 2014), phenols (Aragão et al., 2017; Gao et al., 2016; Zheng et al., 2016), inorganic anions (Liang et al., 2016; Bujes-Garrido and Arcos-Martínez, 2016; Cinti et al., 2016), as far as microorganism's species (Kim et al., 2015a), and their metabolites (Han et al., 2013) in drinking water with dynamic electrochemical methods was also reported.

The main advantage of potentiometric sensors lies in the fact that they do not modify or irreversibly destruct analyzed sample, as it happens when dynamic electrochemical methods (amperometric sensors) are employed. This might be important in the analysis of natural product, including potable water, where an application of dynamic techniques (voltammetry, polarography, etc.) may cause potentially dangerous oxidation of present organic substances or metal/inorganic species reduction. For this reason, potentiometric sensors were widely applied to the analysis of environmental samples (Pankratova et al., 2015). In particular, in potable water potentiometric sensors were applied to the detection of heavy metals (Zhou et al., 2014), surfactants (Makarova and Kulapina, 2017), overall water toxicity (Kirsanov et al., 2014), algal toxins (microcystins in particular) (Lvova et al., 2016; Panchuk et al., 2016).

7.2.2 Optical Sensors

In optical sensors, the optical property of a receptor is altered by the interaction with analytes (Hulanichi et al., 1991). Optical properties include the light-receptor interaction, for instance the spectral absorbance, or the spectral emission of fluorescent, phosphorescent, or chemi-/bioluminescent receptors. In each of these properties a relationship between the intensity of photons flux and the chemical reaction rates can be assessed.

The growing interest in optical sensors is due to the simplicity in preparation, reasonable selectivity, and improved sensitivity of such devices. Moreover, the construction of optical sensors is much simpler respect to electrochemical sensors, since they do not require a sophisticated hardware and wire connections with the detector. Furthermore, their response may be recorded with the optical appliances available in many electronic commodities (like smartphones, tablets, computers) and sometimes without any power supply (while functioning in “naked-eye” mode).

Several optical chemical sensors have been developed for potable water quality assessment. The main attention was paid on the development of sensors for heavy metals [mercury (Long et al., 2017; Yao et al., 2016; Zhu et al., 2015; Bazzicalupi et al., 2013; Piyanuch et al., 2016; Yang et al., 2016), cadmium (Moersilah Siswanta and Mudasir Roto, 2017), lead (Park et al., 2015)], bacteria (Singh et al., 2015), organic pollutants, such as bisphenol A (Wu et al., 2015; Yildirim et al., 2014), aromatics (Xing et al., 2017), dibutyl phthalate (Zhou et al., 2017), organophosphorus pesticides (Kim et al., 2015b; Nsibande and Forbes, 2016; Bai et al., 2015), hydrocarbons (Heath et al., 2017), phenolic-nitroaromatic explosives (Shanmugaraju et al., 2017), dissolved organic mutter and disinfection by-products (Li et al., 2016), and inorganic anions (Ren et al., 2015; Kondekar et al., 2015; Lin et al., 2015a).

Many works also report the possibility of simultaneous monitoring of several pollutants during the same sensing event, by measuring the optical response of the sensing material at different wavelength or by different optical modalities (i.e., colorimetric and fluorimetric) (Shenashen et al., 2013; Na et al., 2015). Thus, for instance, Shenashen et al. (2013) have reported a mesoporous aluminosilicate pellets functionalized with porphyrins for the monitoring and removal of ultratrace levels of Hg(II), Cu(II), and Cd(II), from aqueous media. The reflectance spectra of porphyrin-metal complexes measured at 552, 620, and 636 nm have permitted to assess Cu^{2+}, Cd^{2+}, and Hg^{2+} ions, respectively. Na et al. (2015) have developed a dual-channel colorimetric and fluorescent sensor, based on 4-diethylaminosalicylaldehyde moieties, for colorimetric sensing of copper (II) ion, by changing color from colorless to yellow in aqueous solution, and for fluorimetric detection of fluoride anion. A simultaneous monitoring of biofilm growth, microbial activity, and inorganic deposits on surfaces was performed by means of optical sensor based on multiple fluorescence excitation emission matrix analysis in Strathmann et al. (2013). The sensor employed autofluorescence of amino acids as indicators of biomass and was able to provide an early warning of biofouling.

7.2.3 Gravimetric and Other Types of Sensors

In gravimetric sensors, the accumulation of the analyte on a piezoelectric transducer modified with sensitive film causes a change of the mass graviting onto the surface and then a consequence variation of the resonant frequency of vibration. Recently surface acoustic wave (SAW) sensors for quantification of aromatic hydrocarbons in water have been reported (Sothivelr et al., 2016). Other types of sensor used for assessment of drinking water quality are capacitive (Idil et al., 2017) and chemoresistive devices (Salunke et al., 2017).

7.2.4 Multisensors Approach

The use of sensors and sensor networks by companies that control water quality can help to develop effective early warning systems (EWSs) (United States Environmental Protection Agency, 2005). In addition, the use of a set of selective sensors able to detect particular individual pollution markers, and low selective ones, capable of detecting any contamination, allow us to provide instantaneous “alarm-like” nonspecific information on the status of analyzed water source. The EWS system should be able to give immediate answers, include a wide range of potential pollutants, have a good level of automation, be of simple use, identify the source of a contaminating substance, and allow us to predict the location and concentration downstream of the detection point, be sufficiently sensitive to the detection of pollutants, minimize the number of false positives and false negatives, be robust enough to operate in water, allow remote operations and adjustments; always work and be open to third-party verification and evaluation examinations.

Different from individual single sensors, which provide a single data reading, in multisensors analysis, the output of a sensor array is a vector or a matrix. The chemometric analysis is necessary to interpret the information obtained from the sensor array, and to correlate it with the content of the sample (Lvova et al., 2014). Calibration models are then used to either directly predict the concentration of species under interest, or to evaluate some related parameters, such as, for instance, degree of pollution, hardness, toxicity, etc. The most often applied chemometric techniques used in multisensors analysis are PCA, DA, and various regression methods, for instance partial least squares (PLS) regression, principal component regression (PCR), etc. (Esbensen, 2004).

Several examples of sensor systems implementation for on site or remote water quality monitoring have been reported in the literature (Winquist et al., 2011; Capella et al., 2010; Martínez-Mañez et al., 2005a,b; Campos et al., 2012; Krantz-Rülcker et al., 2001; Eriksson et al., 2011). Thus, a wireless remote-control system based on ion-selective electrodes (ISEs) for ammonium ion, chloride, and nitrate analytes has been installed in the water withdrawal and distribution system for human consumption in the area of Lake Albufera, Spain (Capella et al., 2010). The system was composed of single nodes, formed by the block of the three sensors. Communication between the nodes was done through a telephone operator using proprietary wireless networks and secondary data transmission services (GSM or GPRS), Fig. 7.1.

The sensor signals were integrated and preserved in the control center, from where the data could be extracted via Internet services for further analysis and conclusions. The results obtained from online measurements with ISE sensors were compared with standard reference methods: cadmium nitrate reduction, salicylate-hypochlorite (indophenol) spectrophotometric method for ammonium ion detection, argentometric titration according to Mohr for chloride ion (American Public Health Association, 1998). The system was flexible, requiring very little maintenance and proved promising to be used for monitoring drinkable water quality. A multisensor system for water quality measurement, using thick-film technology procedures on an alumina substrate has been developed in Martínez-Mañez et al. (2005a). The device was able to simultaneously measure pH, temperature, DO, conductivity, redox potential, and turbidity; moreover, the graphite conductive sites were introduced in the sensor array for further possible deposition of polymeric membrane electrodes, Fig. 7.2.

The group of Winquist group from Linköping University, Sweden reported several applications to drinking water quality monitoring of a voltammetric electronic tongue, based on the array of different inert metal electrodes (Winquist et al., 2011; Vagin et al., 2016; Krantz-Rülcker et al., 2001; Eriksson et al., 2011). Examples of applications are the whole drinking water production cycle (Krantz-Rülcker et al., 2001), water quality monitoring on site (Winquist et al., 2011), and remote monitoring (Eriksson et al., 2011).

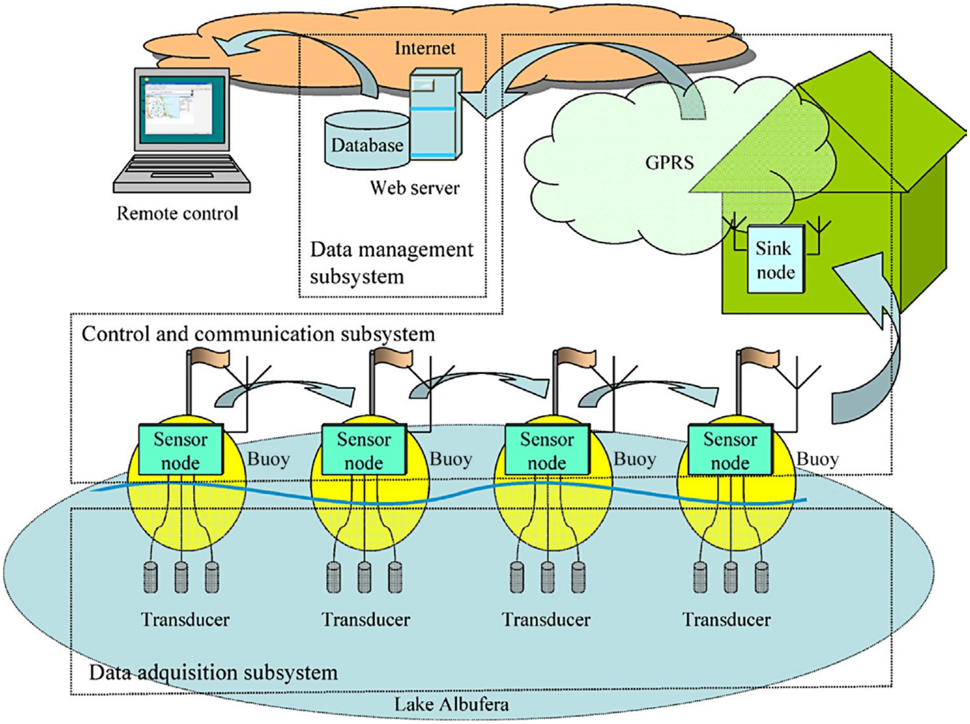

Fig. 7.1 The architecture of the monitoring system of water intended for human consumption developed in Capella et al. (2010). Reprinted with Elsevier permission.

Potentiometric “electronic tongue” systems using various sensitive materials and biosensors have been developed for on-site application for the analysis of various matrices, including potable water (Legin et al., 2000; Mimendia et al., 2010; Men et al., 2005; Riul et al., 2010).

An electronic nose device was developed by Sberveglieri et al. for the detection of microorganism in water and different food matrix (Sberveglieri et al., 2015). Immunochromatographic assay for the simultaneous detection of several chemicals [lead(II), microcystin-LR, chloramphenicol, testosterone, and chlorothalonil] in drinkable water was reported by Xing et al. (2015). For the scope, five antigens were immobilized on separated test lines of nitrocellulose membrane. The recognition event was completed by monoclonal antibodies, which specifically recognized the corresponding antigens. The system was able to detect all pollutants at low concentrations, was fast (within 25 min) and permitted to perform semiquantitative naked eye detection, Fig. 7.3.

Optical sensor arrays for the recognition of different drugs in water (Han et al., 2017), inorganic anions (Lin et al., 2015b), and heavy metal cations (Xu et al., 2014) were also reported. Thus Han et al. (2017) have

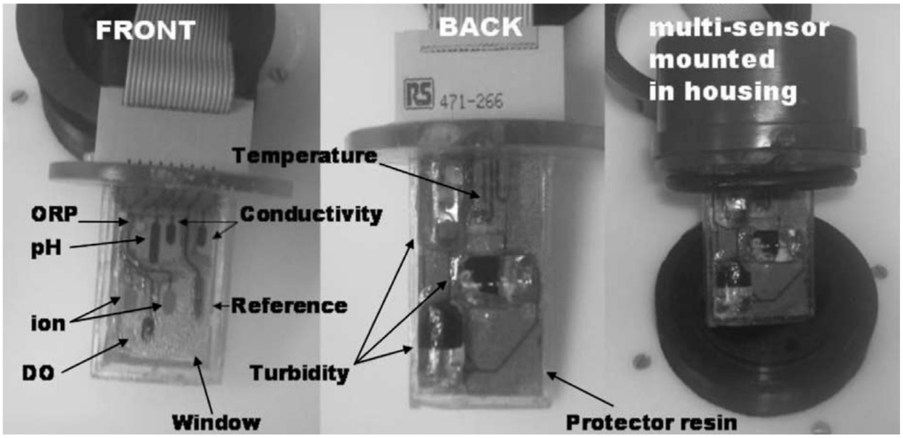

Fig. 7.2 The water quality sensor, based on thick-film technology developed in Martínez-Mañez et al. (2005a). Reprinted with Elsevier permission.

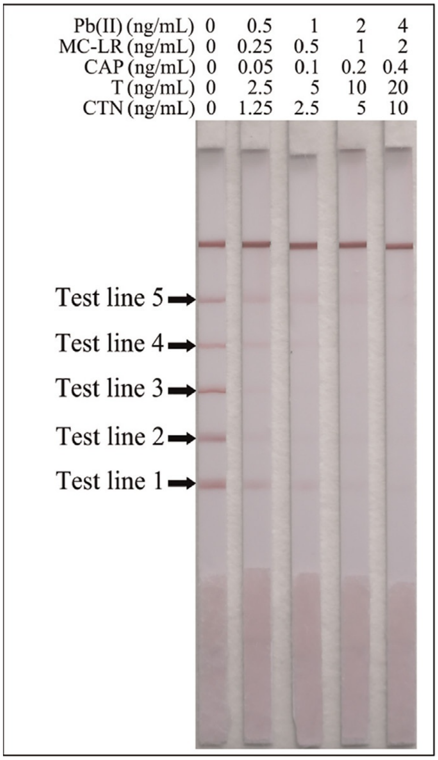

Fig. 7.3 The image of developed in Xing et al. (2015) sensory system for drinking water analysis. On figure: *MC-LR*, microcystin-LR; *CAP*, chloramphenicol; *T*, testosterone; *CNT*, chlorothalonil. Reprinted with Elsevier permission.

shown the possibility to distinguish between original and counterfeit nonsteroidal antiinflammatory drugs (aspirin, ibuprofen, diclofenac, or naproxen) by poly(para-phenylene ethynylene)-based sensor array and chemometric linear discriminant analysis (LDA). A fluorescent sensor array based on supramolecular metallogels for identification of CN^-, SCN^-, S^{2-}, and I^- anions in water was reported by Lin et al. (2015b). The sensor array realized the anion selective response properties by the competitive coordination of the special gelator compound, different metal ions and anions, Fig. 7.4.

Fluorescent sensors based on picoline, quinoline, and BODIPY fluorophores for selective multicomponent detection of cations, such as Zn^{2+}, Cu^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+}, Pb^{2+}, and Cd^{2+}, was reported in Xu et al. (2014). A PCA analysis of these fluorophore responses in PBS upon addition of metals measured with SpectraMax M2 plate reader shown the possibility to perform a quantitative identification of each heavy metal ion.

Bioelectronic tongues based on different types of biosensors were used for the measurement of water, wastewater, and food samples quality (Czolkos et al., 2016; Cetó et al., 2016). Applications of biochips modified with different cells or microorganisms for the evaluation of toxicity of drinking water samples were also reported by several researches (Brennan et al., 2016; Mankiewicz-Boczek et al., 2015; Eltzov et al., 2015; Widder et al., 2015; Queirós et al., 2013; Zhao and Dong, 2013). An interesting application of genome-wide bacterial sensor array for "barcoding" of water pollutants was reported by Elad and Belkin (2013). On the contrary, the amount of works involving the application of nonenzymatic low-selective E-tongue devices and multisensors for the environmental monitoring purposes and in particular for evaluation of water toxicity is far

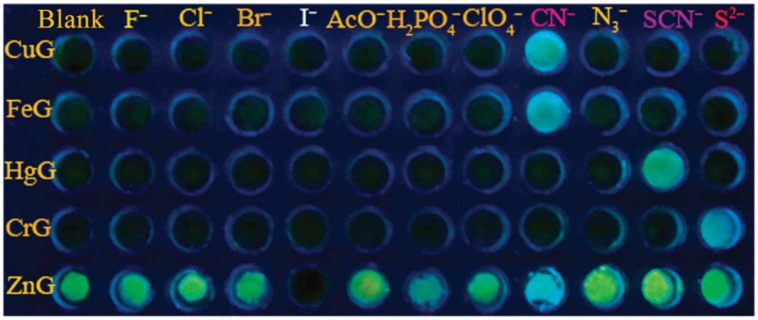

Fig. 7.4 Fluorescence responses of sensor array toward one equivalent of various anions. Reprinted from Lin, Q., Lu, T.-T., Zhu, X., Sun, B., Yang, Q.-P., Wei, T.-B., Zhang, Y.-M., 2015. A novel supramolecular metallogel-based high-resolution anion sensor array. Chem. Commun. 51, 1635–1638 with permission of Royal Society of Chemistry.

to be numerous (Smeti et al., 2009; Lvova et al., 2016; Panchuk et al., 2016; Zadorozhnaya et al., 2015; Heras et al., 2010).

In our laboratories we have recently demonstrated the utility of potentiometric, optical, and multitransduction sensor arrays for the evaluation of microcystine-LR (cyanobacterial hepatotoxin), heavy metals, and several common potable water contaminants (pesticides, inorganic anions, etc.).

We describe below three case studies devoted to these recent applications on E-tongue systems are discussed in details in order to illustrate the ability of multisensor systems to address real-world analytical tasks.

7.3 Case Study 1: Potentiometric E-tongue for MC-LR Screening in Drinking Water

7.3.1 Case Statement

An important task in quality assessment of surface and drinking water is the monitoring of cyanobacteria spread and the release of toxic products of their vital activity, microcystins in particular (Lvova et al., 2016; Panchuk et al., 2016). Microcystin-LR (MC-LR), one of the most poisonous among cyanobacteria toxins, belongs to a family of hepatotoxic cyclic heptapeptides. Being the protein phosphatases (PP1A and PP2A) inhibitor, MC-LR is considered a tumor promoter, since it affects the normal functioning of the liver and is responsible for acute and chronic poisoning phenomena in animals and humans, even when present in nanomolar concentrations. A maximum limit for MC-LR in drinking water is fixed by WHO to 1 μg/L (WHO, 2011). The detection of MC-LR in natural and potable waters became extremely important. Standard instrumental methods for MCs analysis are based on separation methods, such as liquid chromatography (LC) in combination with mass spectrometry or fluorimetry (Meriluoto et al., 2000). Sensor platforms using enzymes are also widely used (Campas et al., 2007; Zeck et al., 2001; Singh et al., 2012). The main disadvantages of the above methods are the need for special and expensive equipment for instrumental analysis, while the instability of enzymes limits the capabilities of enzyme sensors. In this regard, the development of inexpensive and labor-intensive analytical systems capable of performing a fast and reliable assessment of MC-LR toxicity in water samples is of high interest. In this case study we evaluate the possibility of assessment of MC-LR content in drinking water by means of nonenzymatic potentiometric sensor array, as effective, simple to use, and inexpensive alternative to the instrumental analytical methods and enzymatic- and immune-biosensors.

7.3.2 Experimental

A multisensor system made of eight potentiometric sensors containing electrodes was used in this work for the detection of MC-LR in water and recognition of various strains (toxic, TOX, and nontoxic, NTOX) of blue-green cyanobacteria *Microcystis aeruginosa*.

Several types of sensors were included in the potentiometric E-tongue system: PVC-based solvent polymeric membranes doped with Co(TPP)Cl (sensor A1) and nonactin (sensor C1) ionophores, ion-exchangers TpClPBK (sensor C2), and $TDANO_3$ (sensor A2); chalcogenide glass sensors (CG-Cu, CG-Pb, CG-Ag) and polycrystalline sensor based on LaF_3 (sensor A3). The PVC-based solvent polymeric membrane cocktails were formed according to the standard method reported elsewhere (Lvova et al., 2013a). Chalcogenide glass and polycrystalline sensors were from Sensor Systems (St. Petersburg, Russia).

The response of the E-tongue to MC-LR was tested in 10^{-10}–10^{-8} mol/L aqueous calibration solutions, prepared by addition of calculated amounts of 10^{-6} mol/L stock solution of MC-LR in methanol to tap water (Tor Vergata zone, Rome, Italy). Samples of tap water and natural waters, contaminated with aliquots of the inorganic nutrient medium of the reactor and where TOX and NTOX strains of *M. aeruginosa* algae were grown were studied during a 3-month period. Sampling was carried out twice a week; the portions were tested in seven different dilutions, so the number of samples examined was 168 for each strain. All samples were examined using a multisensor system, and the content of MC_LR in them was carried out using a standard HPLC-DAD method with a fluorometric termination and using a colorimetric enzyme method based on suppression of the activity of protein phosphatase-2A (PP2A). PCA, PLR method, and PLS-DA were employed for E-tongue data treatment.

To estimate the success of constructed PLS models, the leave-one-out cross-validation was implemented, given the small sample set available. The RMSEV (root-mean-square error of validation) and the correlation coefficient of predicted versus measured correlation line, R^2, were used as PLS models' predictive ability. Multivariate data analysis was performed with Unscrambler software (v. 9.1, 2004, CAMO PROCESS AS).

7.3.3 Results

The study of E-tongue sensors response to growing amounts of TOX M. aeruginosa filtrate spiked in tap water has indicated a significant sensors sensitivity be attributed to the change of chemical composition of the media, and in particular to the algae MC-LR release, Fig. 7.5. In order to obtain a correlation between the response of the array of sensors and the reference HPLC data on the concentration

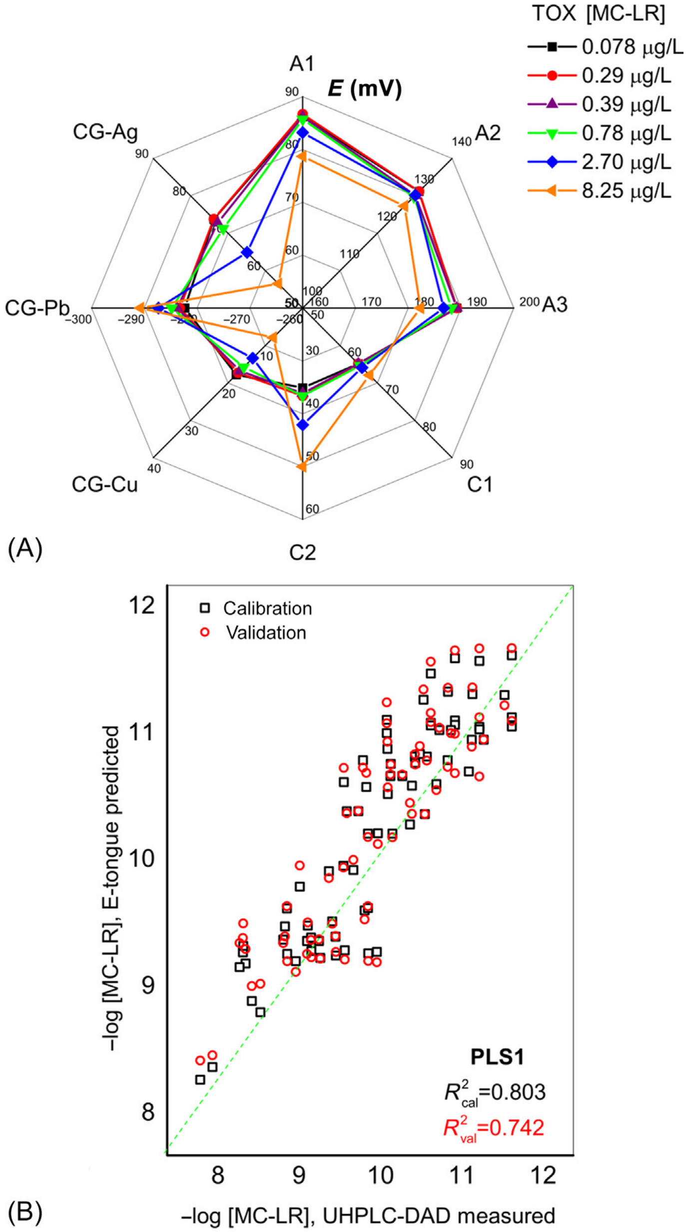

Fig. 7.5 (A) The responses of potentiometric sensors in tap water spiked TOX M. aeruginosa strains. (B) PLS correlation result for MCs content determined by means of potentiometric E-tongue system. Reprinted from Lvova, L., Guanais Gonçalves, C., Petropoulos, K., Micheli, L., Volpe, G., Kirsanov, D., Legin, A., Viaggiu, E., Congestri, R., Guzzella, L., Pozzoni, F., Palleschi, G., Di Natale, C., Paolesse, R., 2016. Electronic tongue for microcystins screening in waters. Biosens. Bioelectron. 80, 154–160 with Elsevier permission.

of MC-LR in the studied filtrates, the method of PLS1 was used. The most representative periods, corresponding to the initial step of algae growth with low content of released toxin, and the final step when a sharp increase of MC-LR production followed by the decline phase related to the cyanobacteria aging and death, were chosen in order to estimate the success of E-tongue in MC-LR concentration prediction.

The coefficient of correlation of the linear relationship between the response of the E-tongue and the logarithm of the known concentration of MC-LR evaluated by full cross validation was close to unity value and amounted to $R^2=0.742$. The root-mean-square prediction deviation, RMSEV, was 0.49 units in the logarithmic scale of the MC concentration. The detection limit of the MC of 0.014 μg/L was estimated using the 3σ ($\mathrm{IF}=3\sigma/S$ method, where σ is the mean-squared error of calibration, RMSEC calculated in μg/L, and S is the slope of the regression curve at the calibration stage, 0.803). The result obtained was promising, since the obtained detection limit was several times lower, then WHO guideline value of 1 μg/L, and considering the complexity of the analytical task.

The chemometric correction of sensor response drift over time was carried out by splitting the array of data, measured by the potentiometric multisensor system during the entire period of growth of cyanobacteria, into two subarrays corresponding to two different phases of their growth: samples with a low MC-LR content (1.9–8.3 μg/L), collected during the first month of growth, as well as samples with a significant MC-LR content (28–300 μg/L). Taking into account the successive dilutions of *M. aeruginosa* strains in drinking water (in ratios 1:3333, 1:1666, 1:1000, 1:500, 1:100, 1:20), data set with low and high MC-LR consisted of 45 and 60 samples, respectively. In each set, 15 or 20 samples (one-third of the total number) were arbitrarily chosen as test simulations for the PLS. The remaining samples were used for calibration. The random splitting procedure was repeated 20 times for both low and high MCs content data sets. To evaluate the constructed PLS models, RMSEV values were averaged over the splits and resulted values were 0.231 and 0.035 μg/L of MC-LR, determined with enzymatic and UHPLC-DAD methods for “low” and 1.181 and 0.297 μg/L for “high” sample sets, correspondingly.

It was also shown the possibility of discrimination among TOX and NTOX strains of M. *a*eruginosa using PLS-DA method. Among 40 samples subject to classification (23 filtrates of the TOX strain and 17 of the NTOX filtrate), a correct classification was obtained for 65% of the samples, and this preliminary result is satisfactory, given the small set of data being processed. The application of mathematical methods to correct in time the sensor response drift made possible to achieve a 100% correct PLS-DA classification of all tested M. aeruginosa strains.

7.3.4 Outline

Satisfactory correlation coefficient, RMSEV lower than the WHO guideline values for microcystin in drinking water, and 100% classification of the toxic and nontoxic strains of M. aeruginosa by means of the developed potentiometric E-tongue open up new perspectives for the application of such multisensors system in the field of environmental monitoring.

7.4 Case Study 2: Detection of Diverse Threats in Potable Water With Optical Sensor Arrays

7.4.1 Case Statement

In this case study we investigated the sensitivity of an array of chemoresponsive dyes, consisting of metalloporphyrins and pH indicators, differently blended with ionic exchanger salts and between them (Guanais Goncalves et al., 2016). The array is applied to the identification in water of a set of noxious compounds that can be used for intentional contamination of potable waters. Water distribution systems are rather vulnerable to deliberate contamination, having many potential entry points accessible for rapid and extensive spread of harmful compounds (Meinhardt, 2005). Chemicals normally used in agriculture, medicine, and industry are easily accessible, even in large quantities, and can be used for the scope. The chemical properties of such compounds are sparse and then it is not realistic to plan a monitoring system based only on selective sensors. On the other hand, since the water in municipal networks is, to certain extent, rather homogeneous, it may be devised a system able to give alarm signals upon detection of deviations from the normal water composition. The main purpose of this current study was to investigate if different classes of organic pollutants/poisons can be detected with a colorimetric sensor array and to investigate how the different indicators contribute to the obtained data. Among the manifold of toxic compounds, six substances representative of pesticides, drugs, and intermediate products in the chemical industry were considered. The tested compounds are: cyclohexanone, dimethylmethylphosphonate (DMMP), piperazine, imidacloprid, 5-fluorouracil (5-FU), and paraoxon.

7.4.2 Experimental

The compounds were tested at concentrations approximately in the range from 10^{-7} mol/L to 10^{-4} mol/L in a background of drinkable water. Ten different sensing materials were prepared by varied combination of three different ingredients: porphyrin, pH indicator, and ion-exchanger salt. Manganese and cobalt complexes of tetraphenylporphyrin, phenol red (PR), and bromocresol purple (BCP) as pH indicators, tridodecylmethylammonium chloride (TDMAC) anion-exchanger, and potassium tetrakis(4-chlorophenyl)borate (TcP) cation-exchanger were incorporated in PVC/DOS (1:2 by weight) polymeric membrane and spotted on Thermanox plastic coverslip (Nunc).

The camera measures the light reflected by the substrate surface. The PhilipsSPC900NC/00 camera operated at the resolution of 320 × 240 pixels connected via USB to the computer was used as optical signal detector; the red, green, and blue LED emitters of ASMT series (Avago technologies) were used as light sources. The measurement cell was a plastic Petri dish, the substrate was fixed on the bottom of the dish that was filled with the water. The analytes were then spiked in the Petri dish at known concentrations. In order to measure the color changes, the sensitive spots were sequentially illuminated with red, green, and blue LEDs. All the measurements were made in triplicate. At each illumination the camera recorded an image. The images were stored in jpeg format, thus each pixel was characterized by a triplet of RGB values from 0 to 254. The values of red, green, and blue channels were considered for the corresponding illuminating color. The sensors sensitivity was calculated as the slope of the response curves in the semi-log plots toward each tested compound. The measurement set-up is shown in Fig. 7.6. PCA was employed for E-tongue data treatment. Multivariate data analysis was performed with MATLAB software MATLAB (v.7.9, 2010b, The MathWorks, Inc., Natick, USA).

7.4.3 Results

Results show that all tested sensing materials are sensitive, although scarcely selective to the tested compounds. Their selectivity patterns are, however, sufficiently different to enable multivariate identification of compounds, independently from the concentration in water.

The PCA has been calculated on a matrix of 30 sensor signals and 30 measurement rows (five concentrations for each compound). First principal component, PC1 (55.7% of total variance) was sensitive almost only to the quantitative aspects of the samples, with no selectivity regarding the nature of the compound. On the contrary, the other principal components have shown a separation of the data according to the kind of compound: PC2 (25.2% of total variance) discriminated 5-FU, PC3 (8.5% of total variance) segregated imidacloprid, piperazine was distanced from the other compounds by PC4 (4.3% of total variance), and paraoxon by PC5 (2.3% of total variance). Moreover, the clear separation among the compounds was obtained on the PCA score plot of the first three PCs, where the lines of growing concentrations of each compound point in a different direction of the three-dimensional (3D) space, Fig. 7.6C.

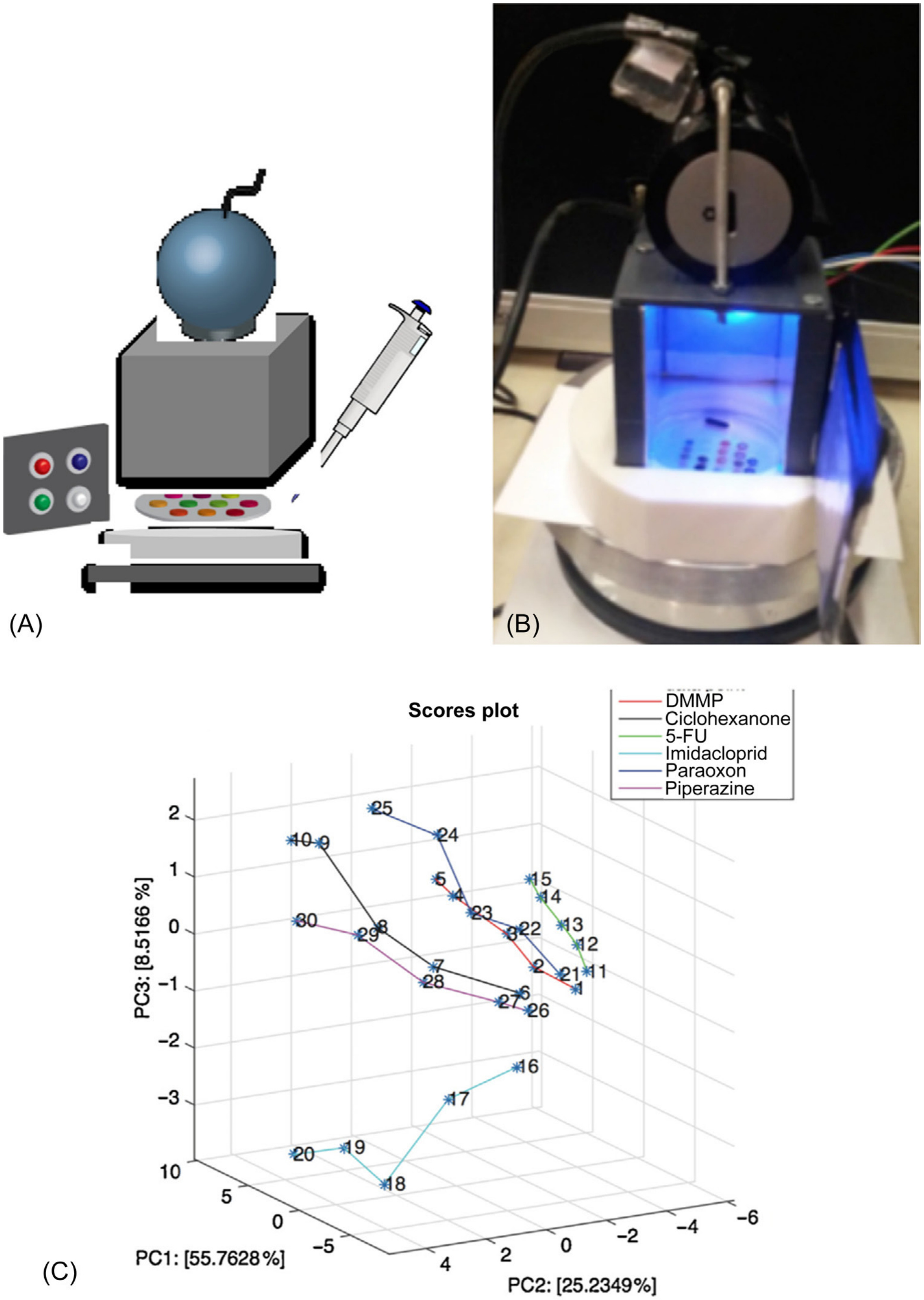

Fig. 7.6 (A) The scheme of measurement set-up; (B) picture of the experimental setup under blue illumination; (C) PCA scores plot of PC1, PC2, and PC3 of optical sensor array response toward six tested treats in drinking water. Reprinted from Guanais Goncalves, C., Dini, F., Martinelli, E., Catini, A., Lundström, I., Paolesse, R., Di Natale, C., 2016. Detection of diverse potential threats in water with an array of optical sensors. Sens. Actuators B 236, 997–1004 with Elsevier permission.

7.4.4 Outline

It was demonstrated that the arrays of optical sensors based on blends of chemical indicators are effective for the identification and recognition of patterns of potentially dangerous compounds in drinking water and relevant for medical, food, and environmental applications. The chemistry of acid/base indicators makes the sensitivity of these materials well beyond the simple pH. The blending of porphyrins and pH indicators offers a further degree of freedom for the preparation of sensing materials. Such multisensor systems are well complement to the ready-to-use optical platforms found in devices such as smartphones, tablets, and computers. In practice it is of interest to have an early indication that something unexpected has happened in the distribution system, which can be followed up with a careful analysis of the cause of the event, so allowing prompt remediation procedures.

7.5 Case Study 3: Multitransduction Sensory System for the Assessment of Transition Metals in Drinking Water

7.5.1 Case Statement

Heavy metals are natural components of the earth's crust that are not degraded by biological and photochemical activity and cannot be disposed. Once released into the environment, heavy metals can remain for hundreds of years. Some natural phenomena such as volcanic eruptions, forest fires, and tides contribute to natural cycling of heavy metals, but unfortunately nowadays human beings rather than nature play a crucial role in altering the rate of release and transport of heavy metals in the environment and increase their emissions to several orders of magnitude. Among the various heavy metals, the metals with potential toxicity, but nevertheless indispensable for living organisms are: cobalt, chromium, copper, manganese, molybdenum, selenium, and zinc. Aluminum, arsenic, beryllium, cadmium, mercury, nickel, and lead of metals are considered predominantly toxic. The WHO recommended that the maximum safety level of most toxic metals should not exceed 0.005 mg/L of Cd^{2+}, 0.01 mg/L of Pb^{2+}, and 0.001 mg/L of Hg^{2+} (WHO, 2011), and the careful monitoring of these pollutants in natural objects, and especially in drinkable water is required.

Despite the big number of selective sensors developed for heavy metals detection in environment, and in drinkable water in particular, many of them suffer from unsatisfactory selectivity, or complicate pretreatment procedures. Moreover, for several transition and heavy metals, no appropriate chemical sensors have been developed yet. An application of multisensors approach was demonstrated to improve significantly the efficiency of the analysis with sensor arrays, thanks to the multiparametric principle (Lvova et al., 2014). Recently the application of multitransduction analysis, as a novel variation of the multisensors approach has been introduced (Lvova et al., 2013b, 2015). In multitransduction sensory system several transduction mechanisms, for instance electrochemical and optical, are employed to the same sensing layer during the same sensing event, thus significantly improving the resolving power and the overall performance. In this way, multitransduction sensory systems could provide sensitive and specific capabilities for a wide range of target analytes and unknown samples that are currently difficult to detect with existing technologies. Another big advantage of multitransduction approach is an opportunity to accomplish an internal calibration and cross-validation of system performance—for example, if the electrochemical part does not work—the optical response can be checked to understand what happened. Although intriguing, only few reports on multitransduction sensing systems can be found in the literature (Wang and Swensen, 2012; USPTO, n.d.). Recently we have shown the utility of such an approach for monitoring of natural waters heavy metal pollution (Lvova et al., 2013b) and here we describe in detail our recent studies in this area.

7.5.2 Experimental

E-tongue array, composed of five PVC-based solvent polymeric membranes M1-M5, doped with two ligands, 5,10,15,20-tetraferrocenyl porphyrin (H_2TFcP) and 5-(7-methoxycoumarin-4-methyl)-2,8-dithia-5-aza-2,6-pyridinophane (L3, the abbreviation employed in our previous studies (Bazzicalupi et al., 2013)). These two compounds were shown to be effective chromophores for the selective fluorimetric detection of transition metal ions, Pb(II) and Hg(II) respectively; while L3 increases the fluorescence with the mercury concentration growth, the H_2TFcP fluorescence quenches under exposure to growing amounts of Pb(II) (Lvova et al., 2013b).

Membranes M1 and M5 contained only one H_2TFcP fluorophore (1% by weight with respect to the membrane weight) and L3 (3% by weight with respect to the membrane mass), respectively; while membranes M2, M3, and M4 were prepared by mixing membrane cocktails M1 and M5 in different proportions: 2:1, 1:1, 1:2 by volume. Lipophilic anionic sites of TpClPB-5% by weight were also included in membranes M1 and M5. For the array thus prepared, simultaneous recording of the potentiometric and CSPT (computer screen photoassisted technique) optical responses was performed. For this, the separate electrical channels for each polymeric film spot were cut out on the unique ITO glass slide; this glass together with a saturated calomel reference electrode was placed in a transparent cuvette containing the analyte solution.

In CSPT measurements E-Tongue was backside illuminated by sequence of 50 colors, generated by TFT-LCD computer monitor screen upon the analyte exposure and registered with a webcam connected to the same computer. CSPT measurements were made using in-house written codes running in MATLAB (v.7.9, 2010b, The MathWorks, Inc., Natick, USA). PCA and PLS methods were employed for E-tongue data treatment. The RMSEV and R^2 values were used as PLS models' predictive ability. Prior to analysis, the mean normalization procedure was applied to treat simultaneously the potentiometric and optical CSPT responses of sensors. Multivariate data analysis was performed with Unscrambler software (v. 9.1, 2004, CAMO PROCESS AS).

The consecutive additions of metal ion species were performed to the water samples coming from Rome water supply system (Tor Vergata, Ciampino, and Pomezia zones, respectively) and three surface water samples (Albano lake, Tiber river and Liri river) in order to simulate pollution situation. The additions were as follows: 0.1 mM of NaCl, 0.1 mM of $CoCl_2$, 0.1 and 1 mM of $Pb(NO_3)_2$, and, finally 0.1 and 1 mM of $HgCl_2$. The calculated aliquots of 1 mM and 1 M stock salt solutions were added to the water samples to obtain the above listed final salt concentrations.

7.5.3 Results

The PCA of potentiometric and CSPT responses of M1-M5 E-tongue array did not show any separation among the contaminated water samples, on the other hand the PCA applied to the hyphenated potentiometric and optical CSPT signals of the Mb1-Mb5 shows a clear separation of all analyzed metal ion species in all tested concentrations, Fig. 7.7 (Lvova et al., 2015).

At the same time, the highest loadings and, therefore, the greatest influence on the discriminating principal components were contributed by membranes M1 and M5 based on individual chromophores. However, PCA of data obtained only with the use of these two membranes functioning in the combined CSPT-potentiometric mode did not successfully identify the water samples contaminated with ions of different metals (data not shown), which indicates the expediency of applying cross-sensitive membranes M2-M4 based on two ionophores TPFc4 and L3 with the opposite luminescent activity for multitransduction monitoring of drinking water pollution.

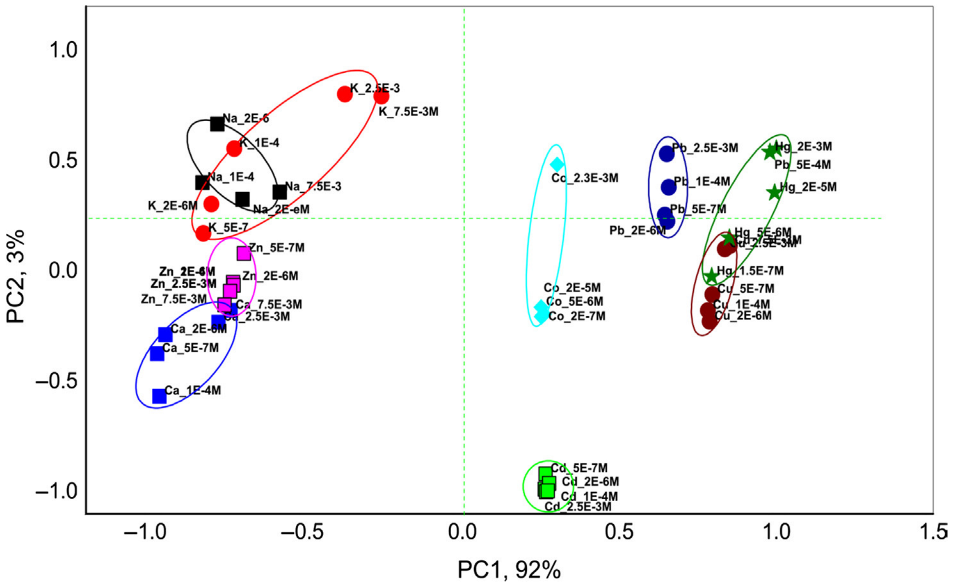

Fig. 7.7 The PCA score plot of CSPT-potentiometric data fusion. Reprinted from Lvova, L., Pudi, R., Galloni, P., Lippolis, V., Di Natale, C., Lundstrom, I., Paolesse, R., 2015. Multi-transduction sensing films for electronic tongue applications. Sens. Actuators B 207B, 1076–1086 with Elsevier permission.

To obtain the correlation between the CSPT-potentiometric response of the developed E-tongue system and the reference data on the metal ion concentrations in calibration solutions, the PLS2 regression method was used. Due to the limited number of samples available, the full cross-validation was applied as resampling validation procedure. The reasonable regression models were obtained for almost all metal ion species, with regression correlation coefficients varied in a range from 0.587 to 0.996 and the RMSEV values of 10 to 10th mM (Lvova et al., 2015). Thus, for instance the linear relationship between the response of the sensors and the lead(II) ions concentration with a correlation coefficient $R^2 = 0.983$ was obtained in the concentration range from 2.7×10^{-7} to 3.0×10^{-3} mol/L. The RMSEV was 3.9 μmol/L, and the lower detection limit of was 0.17 μmol/L, which is found at the level of WHO for Pb^{2+} ions in natural waters (Lvova et al., 2013b).

Finally, the CSPT potentiometric E-tongue was applied for the analysis of drinking and surface waters in Rome area. As it is shown in Fig. 7.8A, by plotting PC1 and PC2 values, which account 91% of total variance, and a clear separation of the data points in two main groups, corresponding to the superficial and potable waters, was obtained. Moreover, the gradient of waters pollution with growing concentrations of transition metal ions can be observed mainly via CSPT optical analysis, Fig. 7.8B.

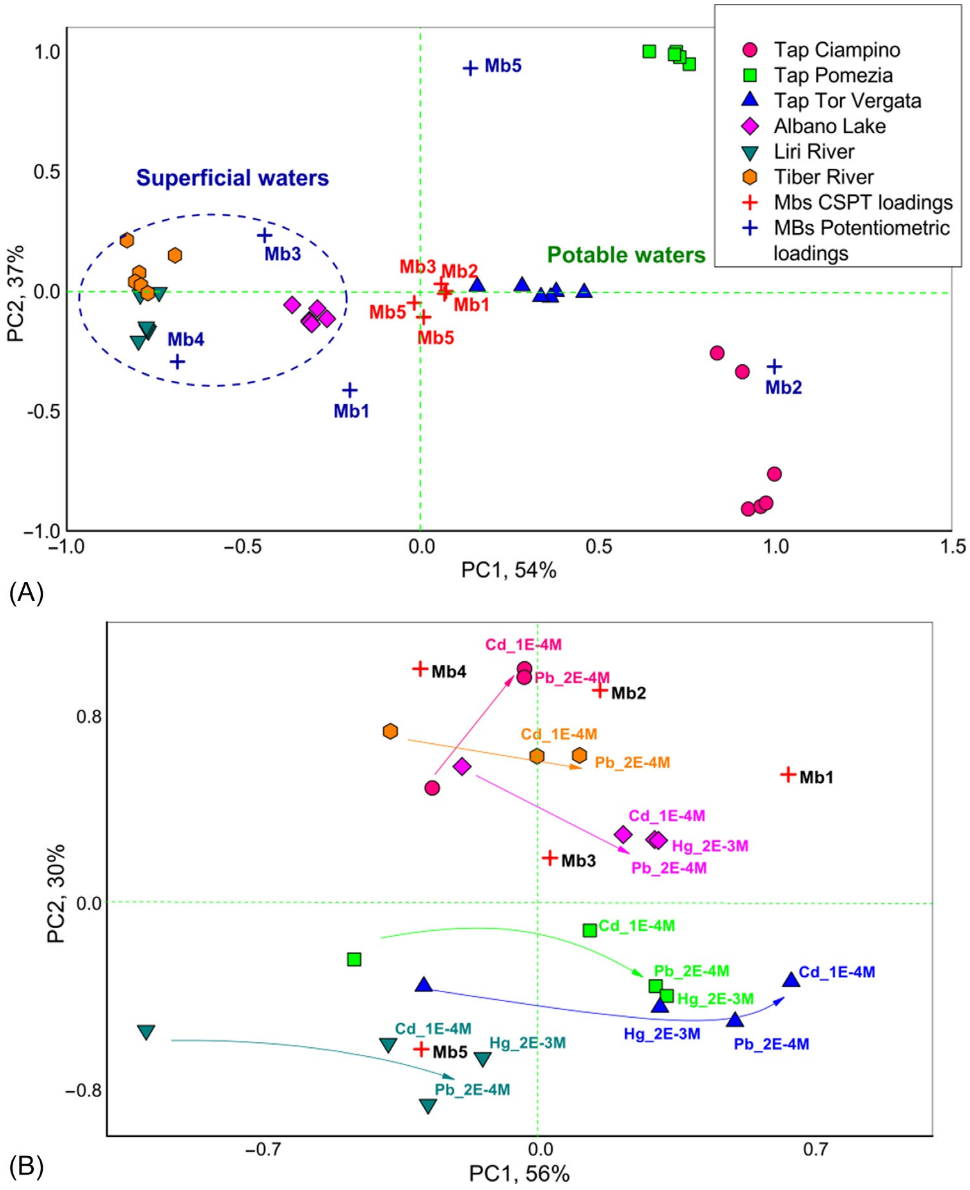

Fig. 7.8 Natural waters analysis by means of CSPT-potentiometric E-tongue: (A) PCA identification of potable and superficial waters; (B) the monitoring of waters pollution with transition metals.

Reprinted from Lvova, L., Pudi, R., Galloni, P., Lippolis, V., Di Natale, C., Lundstrom, I., Paolesse, R., 2015. Multi-transduction sensing films for electronic tongue applications. Sens. Actuators B 207B, 1076–1086 with Elsevier permission.

7.5.4 Outline

The utility of hyphenated multisensors systems for monitoring of natural water pollution by transition metals was demonstrated. The use of the multitransduction approach, where the analyte-sensing layer interactions are transduced by two or more different mechanism, gave the evident increase of the analysis efficiency.

7.6 Conclusions

This chapter described the application of chemical sensors for drinking water quality assessment. Specific examples have shown the obvious advantages of multisensor and multitransduction analytical systems employment to improve the efficiency of analysis. In addition, taking into account the integration of the developed sensor materials into new generation transducers based on transparent, conductive, and flexible materials (e.g., paper, graphene, etc.), their miniaturization, and also due to the low cost of used organic sensitive materials and the use of household electronic devices for registration a useful signal of sensors, this technology has a great potential for the development of economical, portable detectors operating in real-time mode.

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8

MICROBIOLOGICAL AND CHEMICAL CHARACTERIZATION OF BOTTLED WATERS

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8.1 Introduction

Water is the most common substance on Earth, and also an essential constituent for life, participating in the structural organization of biological systems and their metabolic activity.

The proportion of water in an adult human body accounts for 60%–70% of its weight. In young organisms, the proportion of water is even higher reaching to 70%–80% in the newborn. The human organism has permanent physiological needs of about 1–2 L of water per day, satisfied by both water and food containing water consumption.

Besides other aspects, the quality of life can also be quantified through the quantity and quality of water dedicated to human consumption. Hence, taking into account the central role of water in the ecosystem support, the rational management of water resources becomes one of the most important premises of the sustainability of a society.

Over the past decade, the consumption of bottled water had increased worldwide. People prefer to consume bottled water considering it being safer and of superior quality than the tap water. To this opinion contributes the intense publicity made by advertising companies that, through the presented spots, induce the idea that bottled water is pure and clean, being a healthier alternative to tap water. Bottled water is also increasingly accepted as an alternative to soft drinks and

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alcohol, so an explosion of bottled water sales was registered in the last years worldwide.

Bottled water intended for human consumption has to correspond to some physical and chemical, microbiological, and radioactivity parameters required for the category of drinking water from underground sources.

Bottled/conditioned drinking water is bottled in containers with various shapes, size, and composition, hermetically sealed, being clean and suitable for direct consumption without additional treatment.

8.2 Classification and Biology of Bottled Water

There are three main types of bottled water: mineral natural water, spring water, and table water (Mavridou et al., 2008). Springs water is considered underground water that can be used for human consumption in a natural state and bottled at source. Natural mineral water, which is microbiologically pure water and has a certain amount of mineral salts and also originates in a subterranean aquifer, can be exploited and used for consumption. Bottled drinking waters, other than mineral natural waters and spring waters, marketed under the name of groundwater are waters intended for human consumption which may contain minerals naturally or intentionally added and may contain carbon dioxide naturally or deliberately added; they contain no sugars, flavors, or other food products. Numerous studies show that in bottled water heterotrophic bacteria (Mavridou, 1992) and especially different species of the *Pseudomonas* genus could often be encountered in bottled water (Loy et al., 2005). The main bacterial species found in bottled waters are represented by: (i) *autochthonous* aquatic species, characterized by a huge heterogeneity, in general oligotrophic species, which rapidly multiply in bottled water, such as *Acinetobacter*, *Moraxella*, *Aeromonas*, *Xanthomonas* species; (ii) *allochthonous* aquatic species represented by contaminants that get in water during the bottling process. Their survival rate in bottled water is generally poor due to low nutrient content, although some bacteria such as *Pseudomonas aeruginosa* could enter in metabolic latency and survive for a long time (Leclerc and Moreau, 2002). Eucaryotic species were also identified in bottled waters, such as: (i) green algae: *Actinastrum*, *Ankistrodesmus*, *Staurastrum*, *Eudorina*, *Oocystis*, *Scenedesmus*, and *Tetraedron*; (ii) blue-green algae: *Agmenellum*, *Anabaena*, and *Cylindrospermum*; and (iii) diatoms: *Bacillaria*, *Cyclotella*, *Melosira*, and *Synedra*. In a study performed by Mavridou et al., only 60% of the analyzed samples were sterile, the rest being contaminated with *P. aeruginosa* (18%), followed by coliform bacteria (13.3%), such as *Enterococcus* sp. (6%), *Escherichia coli* (1.3%), and other species.

If these microorganisms are not properly removed during processing and bottling, multiplication of bacteria may occur in 1–3 weeks after bottling and the number of bacteria may reach a density up to 10^3–10^4 bacteria/mL at 37°C (Tamagnini and Gonzalez, 1997). In addition to natural contamination, the product may be damaged before reaching the consumer, but the contamination of the product may also be due to the merchant/consumer behavior regarding the storage and handling of the containers. It was observed a greater bacterial density to the samples stored at room temperature (about 20°C). However, a storage at low temperatures, such as refrigeration (4–6°C), does not prevent bacterial multiplication. Photochemical processes also generate molecules with low molecular weight, which are readily biodegradable from high-molecular-weight humic complexes. Also the duration of exposure to certain temperatures is very important (Morita, 1997).

8.3 Microbiological and Physicochemical Parameters Tested for the Assessment of Bottled Water Quality

In Romania, bottled water quality assessment is regulated by the Law 458/2002 regarding quality of drinking water, with subsequent amendments and completions (Ordinance No. 22/2017), Order 341/2007 for the approval of hygiene rules and the procedure for notification of drinking water bottled other than natural mineral waters or spring waters, marketed under the name of mass water, as well as HG 974/2004 for the approval of the norms of surveillance, sanitary inspection, and monitoring of drinking water quality, and for sanitary authorization of production and distribution procedure for drinking water. Bottled water testing evaluates the quality and safety of the product sold (Warburton, 1992).

The microbiological and physicochemical parameters analyzed for bottled waters other than mineral waters are those listed in Tables 1 and 2 of Law 458/2002, drinking water quality, regarding quality of drinking water modified by the Law 22/2017 (Law 458, 2002).

8.3.1 Microbiological Parameters Monitored for Water in Bottles or Other Containers

Most waterborne diseases have as etiological agents microorganisms that populate the human digestive tract and are eliminated in the environment (World Health Organization, 2000). An incident taking place in Portugal, where a cholera epidemic with 2467 hospitalized, who are bacteriologically confirmed cases, and 48 deaths due to source contamination was registered in Blake et al. (1977).

Another important topic is the potential of the normal microbiota to cause illness. It is known that *Aeromonas* sp. is associated with wound infections and can cause diarrhea. Different species of *Pseudomonas* can cause illness. Thus, *Pseudomonas* causes important infections in children with cystic fibrosis (Mitache et al., 2017; Curutiu et al., 2013). *Acinetobacter* sp. is the etiological agent of infections in intensive care units. *Moraxella* causes infections of the upper respiratory tract and eye.

Although most *E. coli* strains are harmless, this strain could exhibit powerful virulence factors and can cause severe illness with a large spectrum of etiologies (Panus et al., 2008; Pănus et al., 2012). Their ability to adhere to abiotic and biotic surfaces is pleading for the potential ability of these strains to colonize human mucosal surfaces and thus to initiate and develop an infectious process sustained by the secretion of soluble enzymes such as lipases and glucosidases (Cernat et al., 2007; Neagu et al., 2017).

The relevance of autochthonous microbiota water for public health can only be determined by epidemiological and experimental studies. Some authors express the concern that opportunistic pathogens from bottled water may be able to infect vulnerable individuals (newborns, AIDS patients, immunosuppressive patients after transplantation). They use bottled water as a safer alternative to tap water. It is known that bottled water is not a sterile product.

The first and most important bacteriological condition of drinking water is the absence of pathogenic enterobacteria. Therefore, the use of microorganisms from intestinal microbiota as indicators of water pollution is a universally accepted consensus for monitoring and assessing the microbiological quality of water (Fewtrell et al., 1997).

E. coli is a Gram-negative aerobic bacterium belonging to the *Enterobacteriaceae* family, lactose-fermentative, oxidase-negative, indole, and β-glucuronidase positive, considered a fecal indicator of water recent contamination with fecal.

The term "coliform bacteria" commonly refers to a particular group of bacteria belonging to the *Enterobacteriaceae* family (including *Escherichia*, *Citrobacter*, *Enterobacter*, and *Klebsiella* genera), characterized as Gram-negative, oxidase-negative bacteria, non-sporulated, able to grow in the presence of bile salts and other surface-active agents, capable of lactose fermentation at 35–37°C, and acid and gas production over 24–48 h. Coliform bacteria are widespread in nature and are not considered to be of direct epidemiological importance for water examination. Although not exclusively of fecal origin, the coliform group is present in large amounts in the feces of human beings and warm-blood animals, which allows its detection even after considerable dilution.

Intestinal enterococci Gram-positive cocci isolated or in short pairs or chains, residents of human and animal intestinal microbiocenosis, immobile, with the ability to reduce triphenyl tetrazolium 2,3,5-chloride to formazan, and to hydrolyze the esculin at 44°C. The main species are *Enterococcus faecalis*, *E. faecium*, *E. durans*, and *E. hirae*. They are considered as fecal pollution indicators, but can be also found in water, soil, where they can survive longer than coliforms.

P. aeruginosa is a Gram-negative, aerobic bacterium, widespread in nature (water, soil), but also frequently isolated from the mucous membranes, skin, and digestive tract of human and animals, becoming an opportunistic pathogen known to cause respiratory system infections, urinary tract infections, dermatitis, soft tissue infections, bacteremia, and a variety of systemic infections, especially in patients with immune deficiency, those with catheters, wounds, or cystic fibrosis. The strains responsible for all these infections can also be spread by other sources such as contaminated water (Kolmos et al., 1993; Marinescu et al., 2015). *P. aeruginosa* is considered a microbiological parameter for bottled water, because it is commonly found in soil, residues in the environment associated with human activity, and also in water (basins, drinking water, etc.), because of its ability to withstand large variations of water temperatures and to resist to the action of disinfectants (Hernandez Duquino and Rosenberg, 1987). Due to its particular feature to grow in water with low nutrient content, *P. aeruginosa* is often monitored as an indicator of other bacterial fecaloid contamination. It is recommended to be monitored as an indicator of sanitary hygiene conditions.

It can produce large amounts of extracellular polysaccharides that protect the bacterial cell from the action of disinfectants. It also has the ability to form biofilms on the surface of the installations consisting of cells attached to each other and also to a surface, embedded in a protective matrix.

Pseudomonas aeruginosa, *P. fluorescens*, and *P. stutzeri* are the most common species isolated from bottled water. Besides them, other species such as *P. pseudomallei*, *P. maltophilia*, *P. acidovorans*, *P. testoalcalis*, *P. putida*, and *P. paucimobilis* can be less often found. A great concern for the medical system and for the public health arises from *Pseudomonas* sp. that exhibited high natural resistance and acquired resistance to many antimicrobial agents.

According to Tamagnini and Gonzalez (1997), *P. aeruginosa* growth dynamics in bottled showed a density of 10^3–10^6 per mL within the first 6 days of bottling which doubled in the next 26 h in the presence of the associated microbiota, or in 3–6 h in sterile water.

8.3.2 Number of Heterotrophic Bacteria Grown at 22°C and 37°C

Heterotrophic bacteria are microorganisms that require organic carbon for growth. Heterotrophic bacteria are naturally present in the environment and can grow in water and on the surfaces (soil and plants) that come in contact with water. It is well known that only a small part of the viable heterotrophic bacteria population could be estimated by counting on an enriched nutrient medium incubated at 22°C and 37°C, most of them, although viable, could not be cultivated on an agar medium.

In some cases, the growth of microorganisms is registered also after water has undergone treatment processes, phenomenon considered in the literature as a "regrowth," or "recurrence." The main determinants of this "recurrence" are temperature, nutrient availability (nutrients can come from the water mass or from materials in contact with water), and the absence of a residual disinfectant.

The number of heterotrophic bacteria in bottled water can reach up to 10,000 cfu/mL. Studies have shown that only 0.048%–4.5% of all bacteria ingested by an individual come from drinking water. Exposure to heterotrophic bacteria is much greater in case of food.

Heterotrophic bacteria isolated from water have very few virulence factors in generally. While heterotrophic bacteria are spread throughout the environment, clinical, and epidemiological evidence is insufficient to assert that these bacteria may pose a health risk. Populations of heterotrophic bacteria in drinking water include a wide range of genres (Lazar et al., 2015). Although most of these microorganisms do not pose a health risk to immunocompetent people, some of the bacteria may behave as opportunistic pathogens.

Increased levels of heterotrophic bacteria can be measured in bottled waters after distribution. Some experts believe that *P. aeruginosa* and the number of colonies are indicators that measure the management processes of bottled water production. The main microbiological parameters of bottled waters and their admitted values are presented in Table 8.1.

Table 8.1 The Main Microbiological Parameters of Bottled Waters and Their Admitted Values

Parameter	**Admitted Values**
Escherichia coli	0/250 mL
Enterococcus sp.	0/250 mL
Pseudomonas aeruginosa	0/250 mL
No. of microorganism grown at 22°C	100 per mL
No. of microorganism grown at 37°C	20 per mL

8.3.3 Physicochemical Parameters Assessed for Water Bottled in Bottles or Other Containers

The main chemical parameters tested for bottled water are listed in Table 8.2.

8.3.3.1 Taste and Smell

The study of *taste* and *smell* of water could present a high degree of subjectivity, but their influence on the use of water is decisive, causing even the exclusion of using the respective water. The taste and smell of water can also serve as indicators of water pollution. The taste of water is given by its chemical content especially by its mineral salts and dissolved gases. The excess or deficiency of some of these

Table 8.2 Chemical Parameters Tested in Water and Their Admitted Values According to Actual Standards

Parameter	Admitted Values	Parameter	Admitted Values
Acrylamide	0.1 μg/L	Copper	0.1 mg/L
Arsenic	10 μg/L	Dichloroethane	3.0 μg/L
Benzene	1.0 μg/L	Epichlorohydrin	0.1 μg/L
Benzo(*a*)pyrene	0.01 μg/L	Fluorine	1.2 μg/L
Boron	1.0 μg/L	Mercury	1.0 μg/L
Bromine	10 μg/L	Nickel	20 μg/L
Cadmium	5 μg/L	Nitrates	50 mg/L
Vinyl chloride	0.50 μg/L	Nitrites	0.50 mg/L
Total cyanides	50 μg/L	Lead	10 μg/L
Free cyanide	10 μg/L	Selenium	10 μg/L
Chromium total	50 μg/L	Stibium	5 μg/L
Tetrachlorethane si Triclorethene (sum of the specified compounds concentrations)	10 μg/L	Hidrocarburi policiclice aromatice: benzo(*b*) fluorantren, benzo(*k*) fluorantren, benzo(*ghi*) perilen, indeno(1,2,3-cd) piren	0.1 μg/L
Pesticides from aldrin, dieldrin, heptachlor, and heptachlor epoxide class	0.1 μg/L	Total pesticide	0.5 μg/L

Continued

Table 8.2 Chemical Parameters Tested in Water and Their Admitted Values According to Actual Standards—cont'd

Parameter	Admitted Values	Parameter	Admitted Values
Total trihalometani (sum of the specified compounds concentrations)	100 μg/L	Sulfur and hydrogen sulphide	100 μg/L
Aluminum	200 μg/L	Turbidity	5 UNT
Ammonium	0.5 mg/L	pH	Between 6.5 and 9.5
Oxidability	5 mg O/L	Natrium	200 mg/L
Total organic carbon	No abnormal modification	Sulfat	250 mg/L
Chloride	250 mg/L	Taste	Acceptable to consumers without any abnormal change
Free residual chlorine	0.5 mg/L at the entrance of network and 0.25 mg/L at the end of the network	Smell	Acceptable to consumers without any abnormal change
Conductivity	2500 μS/cm la 20C	Alfa global activity	0.1 Bq/L
Color	Acceptable to consumers without any abnormal change	Reference total effective dose	0.10 mSv/an
Total hardness	Minimum 5 grade	Beta global activity	1 Bq/L
Iron	200 μg/L	Tritium	100 Bq/L
Manganese	50 μg/L	Zinc	5000 rog/L

components could determine an unpleasant taste of water (fad, salty, bitter, sweety). The odor of water is related to the presence in excess of some natural elements or obtained after water purification, as well as from some transformations to which some chemicals, especially pollutants, are subjected into water.

8.3.3.2 pH

For bottled water, the minimum value of pH can be reduced to 4.5 pH units. For bottled water that naturally contains or is enriched with carbon dioxide, the pH value may be lower. Water producers typically specify the pH of the source and not pH of the sold product. A drinking water with an acidic pH results in dental disease, the most exposed population being the infantile.

8.3.3.3 Hardness

The hardness of water is determined by the calcium, magnesium, iron, and zinc salts, originating from the flow of rainwater through different stones which precipitate when the water is heated. It is therefore not recommended to store the bottled water at high temperatures. In most waters, there are calcium and magnesium salts and in very small quantities other metals. Calcium and magnesium are naturally present in water with varying concentrations and together contribute to the hardness of the water. Medium values are considered the most suitable for consumption. Tap water has high resistance values; most bottled water has less calcium than tap water.

The combination of sodium with chlorides (NaCl) is found in highly diluted water sources. Sodium is a key element in bottled water and is essential for health. In healthy adults, sodium is excreted, but in people with high blood pressure and heart disease, as well as in infants with immature renal system, elevated levels of sodium can cause problems, so diet with a low sodium concentration is recommended.

Fluoride traces are naturally found in many water sources. Fluoride is added to drinking water in certain areas to protect children's teeth. Other studies have shown that fluoride is beneficial to the elderly population by reducing arterial wall rigidity and in the treatment of osteoporosis.

Ammonium is a parameter that indicates recent organic pollution.

Nitrites are formed by the activity of nitrifying bacteria and have toxic action with very serious implications especially on the health of young children.

Heavy metals have a significant toxic effect on the human body, all of them being harmful outside a certain range of acceptable values.

8.4 Analytical Methods Used for Water Testing

While advanced technologies have reduced the risk of contamination with microorganisms of alteration during bottling, the issue of product validity becomes important due to higher production capacity. Thus, a quality control of bottling and the biological stability of drinking water is required.

8.4.1 Microbiological Assays

Two techniques are used to analyze the microbiological parameters of water quality: (i) membrane filtration method for analysis of coliform bacteria, *E. coli*, enterococci, *P. aeruginosa*; and (ii) pour plate method for analysis of number of colonies grown at 22°C and 37°C.

8.4.1.1 Membrane Filtration Method

The membrane filtration is an effective, economical method, at the same time meeting the requirements related to quantitative and reproducible determination of traces of microbiological contamination. The membrane filtration method involves filtering the water sample through a hydrophilic membrane (47 mm Ø) under a negative pressure. The diameter of the 0.45 µm of the membrane pores retains the bacteria from the water. The membrane is placed on a growth medium and incubated at the temperature according the targeted bacteria growth, after that the number of suspected colonies developed on the membrane are counted (Fig. 8.1).

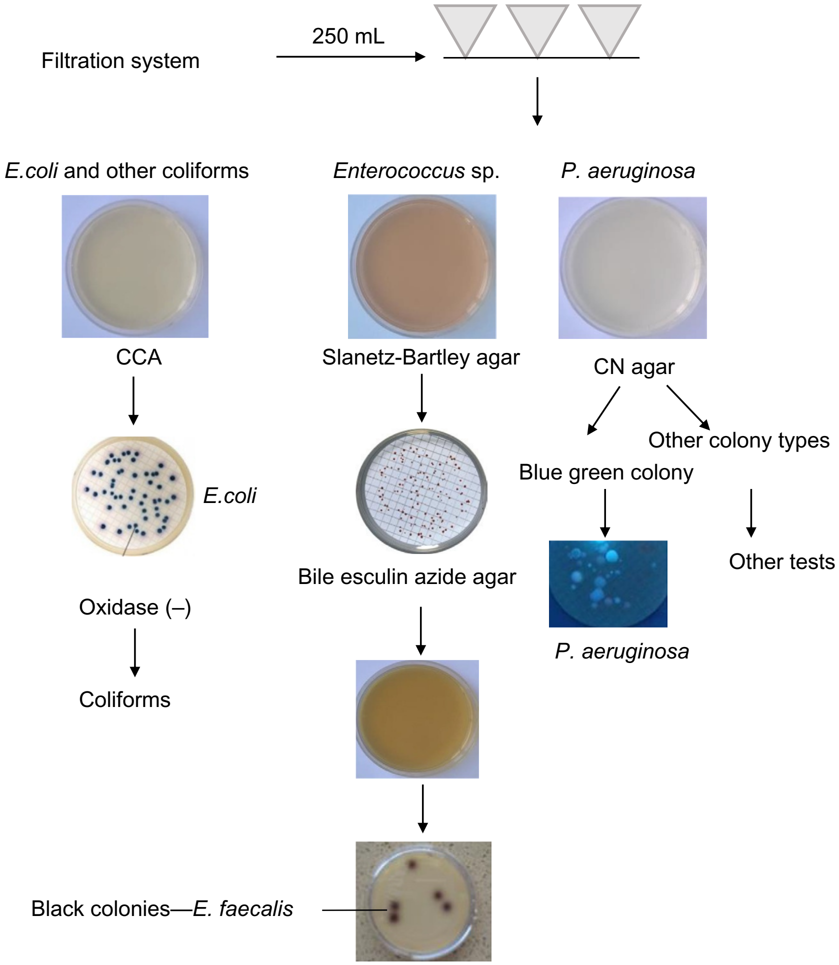

Fig. 8.1 Schematic representation of the microbiological analysis of bottled water (other than mineral and spring water): *Escherichia coli*, coliform bacteria, enterococci, *Pseudomonas aeruginosa*.

By this method larger volumes can be filtered, and the precision of microbiological determinations increases considerably by the concentration effect.

The quantitative results obtained by counting the developed colonies can be reported to the sample volume.

In order to identify *E. coli* and the number of coliform bacteria, the membrane is placed on the CCA culture medium and incubated for 24 h at 36°C ± 2°C. Colonies formed by coliform bacteria are pink to red, and those of *E. coli* are blue (SR EN ISO 9308-1:2015/A1:2017) (Fig. 8.2).

Enterococci that are less susceptible to chemical effects than *E. coli*, being detectable for a longer time (in waste water and chlorinated water) are used as indicators for fecal infestation. Determination of fecal streptococci is performed after incubation of membrane filtration, for 48 h at 36°C ± 2°C, on the Slanetz Bartley medium where they form small black colonies with diameter about 1 mm (SR EN ISO 7899-2, n.d.) (Fig. 8.3).

For detection and enumeration of *P. aeroginosa* on Pseudomonas Agar base/CN-Agar medium, incubation will be performed at 36°C ± 2°C for 48 h. *P. aeruginosa* forms blue colonies of 1–2 mm in diameter with blue halo and lime flower smell. In some cases, the colonies become blue-green, yellow-green, or colorless (SR EN ISO 16266, 2008) (Fig. 8.4).

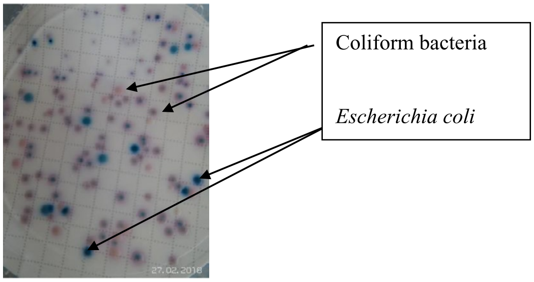

Fig. 8.2 Chromogenic coliform agar.

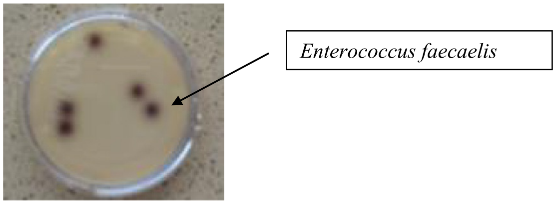

Fig. 8.3 Slanetz Bartley agar.

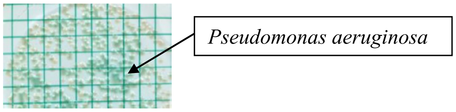

Fig. 8.4 CN agar.

8.4.1.2 Pour Plate Method

It is used to determine the total viable count, the number of microorganisms/mL of a sample by counting the colonies formed on nutrient culture medium with agar after incubation at 36°C and 22°C (SR EN ISO 6222, 2014). It is mainly used for the examination of water intended for human consumption, including bottled waters and natural mineral waters.

8.4.2 Analytical Methods for Assessing the Chemical Parameters of Bottled Waters

8.4.2.1 Electrometric Method

The electrometric method consists in measuring the electromotive force of an electrochemical cell represented by the sample, a glass electrode and a reference electrode. The pH of a sample is temperature dependent, due to the dissociation equilibrium (SR EN ISO 10523, 2012). For this reason the sample temperature is specified along with the pH value. The method is applicable to all types of water samples in the range of 2–12 pH units with a conductivity of <20 mS/cm and in the temperature range from 00°C to 500°C.

In the laboratory, the spectrophotometric method is used to measure the absorbance at 655 nm wavelength of the blue compound formed by the reaction of ammonium with salicylate and hypochlorite ions in the presence of sodium nitrosopentacyanoferrate (sodium nitroprusside) to determine the ammonium content (SR ISO 7150-1, 2001). Due to the harmful effects it can have on the human body, the actual water quality legislation limits the presence of ammonium in drinking water to levels below 0.5 mg/L. By using 10 and 40 mm optical paths, the scope of the method ranging from 0.06 to 1.288 mg/L NH_4^+ was divided into two subdomains, as follows: (i) concentrations in NH_4^+ ions between 0.064 and 0.322 mg/L using a maximum sample volume of 40 mL and 40 mm optic trays; (ii) concentrations in NH_4^+ ions between 0.161 and 1.288 mg/L using a maximum sample volume of 40 mL and 10 mm optical paths. By taking into account smaller sample volumes, higher concentrations can be determined.

Hypochlorite ions are generated by the alkaline hydrolysis of the sodium salt of *N*, *N′*-dichloro-1,3,5-triazine-2,4,6-trione. Chloramine reaction with sodium salicylate occurs at pH 12.6 in the presence of sodium nitroprusside. Consequently, the chloramines present in the sample are quantitatively determined. Sodium citrate is added to mask interference with cations, especially calcium and magnesium.

Determination of the nitrite content (SR EN 26777:2002/C91, 2006) is achieved by the spectrometric method of the molecular absorption based on the reaction of the nitrite ions present in the sample at $pH = 1.9$ with the 4-aminobenzenesulfonamide reagent in the presence of orthophosphoric acid to form a diazonium salt, which in combination with *N* (1-naphthyl)-ethylenediamine dihydrochloride form a colorless red colorimetry complex at 540 nm wavelength. The principle of the method for determining the nitrate content in water is based on the spectrometric measurement of the absorbance of the yellow compound formed by the reaction of the sulphosalicylic acid (resulting from the reaction between sodium salicylate and sulfuric acid) with the nitrate ions followed by alkaline solution treatment. The method is used for concentrations between 0.04 and 0.20 mg/L N (0.18 and 0.89 mg/L NO_3^-) using a maximum sample volume of 25 mL. For larger concentrations, the range can be extended by shrinking the sample volume to a minimum of 0.5 mL. 40 mm optical paths are used for determination. The wavelength to be worked is 415 nm (SR ISO 7890-3, 2000).

For the direct determination of chlorides (SR ISO 9297, 2001) with concentrations between 5 and 150 mg/L and even up to 400 mg/L if a sample dilution is carried out, the content of chlorides dissolved in water is determined by dilution the silver nitrate samples in the presence of potassium chromate as an indicator. The principle of the method consists in the reaction between chloride ions and silver ions to form insoluble silver chloride, evidenced by adding a small excess of silver ions with the formation of yellow-brick silver chromate with chromium ions used as a pH change indicator. During titration, the pH is maintained between 5 and 9.5 to allow precipitation.

The total calcium and magnesium concentration (SR ISO 6059, 2008) represents the total hardness of the water. The carbonate and carbonic content of water is the temporary (carbonate) hardness that is part of the total hardness, while the content of calcium and magnesium ions, other than bicarbonates (sulfates, chlorides, nitrates, etc.) represents the permanent (non-carbonate) hardness of the water. The hardness is expressed in: German hardness grades (10 DH), British hardness grade (0 Clark), French hardness grade (grade F), and American hardness grade (ppm). Determination of the amount of calcium and magnesium concentrations is performed by the EDTA titrimetric method and consists in the titration of calcium and magnesium concentrations with an aqueous solution of ethylenediaminetetraacetic acid (Na_2EDTA) disodium salt at $pH = 10$ in the presence of the indicator black mordant 11. The lowest concentration that can be determined is 0.05 mmol/L (Ca + Mg) equivalent to 0.28 German grades, while the maximum concentration can be 3.6 mmol/L (Ca + Mg) equivalent to 20.2 degrees of German hardness. By separately determining the calcium content (in mg/L) according to STAS 3662/1990 and the sum of the calcium and magnesium ion concentrations according to the present procedure, it is possible to determine the magnesium concentration (in mg/L) in the analyzed sample.

Determination of aluminum content (SR ISO 10566, 2001) is achieved by a spectrometric measurement method at 580 nm wavelength of the blue complex formed by the reaction of aluminum with purple pyrocatechol at a pH of 5.9.

Following the application of the method, both small concentrations of up to 100 μg/L Al^{3+} are determined using 40 mm optical paths and high concentrations up to 500 μg/L Al^{3+} using 10 mm optical paths. It is possible to determine either the soluble (dissolved) aluminum or the acid-soluble aluminum.

Aqueous media reacts with hydrogen ions, a property called alkalinity (SR EN ISO 9963-1, 2002). This is due to the presence in water of bicarbonates, carbonates, and hydroxides, and more rarely of borates, silicates, phosphates, hydrosulfides, etc. Neutralizing a volume of water to be analyzed with a dilute mineral acid, in the presence of a mixture of indicators is the principle of the method. It is designed for natural and treated water and can be used directly for waters with an alkalinity up to 20 mmol/L. The lower alkalinity limit is 0.4 mmol/L. Also, the alkalinity can be expressed in German grades, mg/L HCO_3^-, mg/L $CaCO_3$, using conversion factors.

To determine the content of orthophosphates, total phosphorus, and total dissolved phosphorus, the reaction of orthophosphate ions with an acid solution containing molybdate and antimony ions is used to form an antimony phosphomolybdate complex (SR ISO 6878, 2005). Reduction of the ascorbic acid complex and formation of a blue colored molybdenum complex occurs and the concentration of orthophosphate is determined by measuring the absorption of this complex. Polyphosphates and some organophosphorus compounds are determined if they converted into activated orthophosphate with molybdate formed by hydrolysis of sulfuric acid. Many organophosphorus compounds are converted to orthophosphates by peroxydisulfate mineralization. Mineralization with nitric acid-sulfuric acid is used, but a more energic treatment is needed.

By analyzing a maximum sample volume of 40 mL, phosphorus concentrations between 0.04 and 0.8 mg/L P can be determined using 10 mm optical glass panes and phosphorus concentrations between 0.008 and 0.2 mg/L P using 40 mm glass drum with 40 mm optical path.

To determine the content of cobalt, nickel, chromium, manganese, copper, zinc cadmium, lead, sodium, and potassium, atomic absorption spectrometry is used (SR ISO 8288, 2001; SR EN ISO 5961, 2002; SR EN 1233, 2003). Flame atomic absorption spectrometry is based on the conversion of the sample to the free-atomic level through a atomization process that takes place in the flame (air-acetylene or acetylene-nitrous oxide) followed by specific optical radiation absorption with the length a well-defined wave, radiation emitted by a continuous spectrum source (xenon lamp), and sent to the atomizing source. The absorption of the radiated energy by the atoms is directly proportional to the metal ion concentration in the analyte solution. The wavelength for the maximum absorption signal is specific to each analyzer according to the actual standards and the technical requirements of the spectrophotometer.

To determine the iron content in water, 1,10-phenanthroline must be added to the sample to be analyzed and measured the absorbance of the red-orange colored complex at the wavelength of 510 nm (SR ISO 6332, 1996). For the total iron and total iron dissolved in water, hydroxylamine hydrochloride is added to reduce iron (III) to iron (II). Non-insoluble iron oxides or complexes are dissolved by pretreatment of the samples. The (II)-1,10-phenanthroline iron complex is stable in the pH range of 2.5–9 and the intensity of its coloration is proportional to the amount of iron (II). The relationship between concentration and absorbance is linear up to concentrations of 5 mg iron/L.

By colorimetric dosing at the 540 nm wavelength of the violet colored compound resulting from the reaction of diphenyl carbazide with the chromium ion released by the reaction between the sulfate ion and the barium chromate, the sulfates are directly determined by a molecular absorption reaction (STAS 3069, 1987).

8.5 Conclusions

The risks raised by bottled water poor quality for public health represent an issue intensively debated for a long time. Problems have been raised regarding water contamination with both strictly pathogenic and opportunistic microorganisms. Under improper storage conditions, bacteria can multiply to alarming levels for human health. Recommendations that bottled water is better than tap water for patients with low immune system are supported by the literature. For countries where water quality in public systems is uncertain, bottled water is a safe alternative.

The relatively high frequency of *Pseudomonas* species in bottled waters imposes this parameter to be reconsidered for public health due to the antibiotic resistance commonly encountered in these bacteria. The presence of *P. aeruginosa* in bottled waters is due to contamination during the bottling process or to the water source pollution with organic matter.

Also, nitrate is a hemoglobin-oxidizing agent that can cause methemoglobinemia. The effect of nitrate on infants is well known but less is known about nitrate-induced methemoglobinemia in young children (Kolmos et al., 1993).

Heavy metals, such as cobalt, copper, iron, manganese, molybdenum, zinc are nondegradable and thus can accumulate in the host organisms and cause neurodegenerative diseases. The level of toxicity is closely related to the amount of metals accumulated in the cells, but also to the degree of tolerance of each organism.

In this context, it is necessary to introduce HACCP (Hazard Analysis Critical Control Points) and International Organization for Standardization (ISO) recommendations for the control of production processes to improve the microbiological quality of bottled water.

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9

ADVANCED BIODEGRADABLE MATERIALS FOR WATER AND BEVERAGES PACKAGING

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9.1 Introduction

Conventionally, for bottling water and beverages, polymeric materials and glasses are the main materials used for bottles production, combining excellent mechanical, electrical, and thermal properties with very good chemical resistance and dimensional stability. However, the use of plastic bottles generated big problems, especially because they are not degradable or are difficult to degrade, and the process is time consuming (over 450 years), 50 billion plastic water bottles made of polyethylene terephthalate (PET) being discarded in the environment (Bartolome et al., 2012). Since PET is a polyester with functional ester groups, it can be chemically cleaved by water, alcohols, acids, glycols, and amines, recycling being the only one acceptable according to the principles of "sustainable development," defined by *World Commission on Environment and Development* (1987) as "development that meets the needs of present generation without compromising the ability of future generations to meet their needs" (Bartolome et al., 2012).

The packaging domain is dominated by mineral oil derived polymers (called petroleum-based plastics), like polyethylene (PE) and polystyrene (PS) (Bockhorn et al., 1999; Pathak and Navneet, 2017), and other synthetic materials like polyvinyl chloride (PVC), PS, polyesters (PEs), polyamide (PA), PET, polyolefin (PO), and polyurethane (PU) that have been designed to be resistant to the environment (Tokiwa et al., 2009). Because most of this conventional plastics are nonbiodegradable (Tokiwa and Calabia, 2008), the thermal degradation is

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another approach for their destruction, but the process generates toxic gases such as carbon monoxide (CO) and dioxin ($C_4H_4O_2$), or releases heavy metals (cadmium and lead) through the burning process (Joo et al., 2018). Polymeric materials such as PS, PE, and PP are the most common packaging materials used for soft drink, water, or syrup bottles, and also for yogurt tubs, bottle caps, or coffee cups. The increased use of nonbiodegradable synthetic packaging films led to serious global environment and human health problems (Siracusa et al., 2008).

One of the most discussed chemical compounds that can contaminate the beverages contained by the plastic bottles, with serious implication in the human health is bisphenol A (BPA). The BPA is an estrogen-like chemical which can affect the natural hormonal communication systems when ingested and could contribute to the development of hormone-related cancers (Wang et al., 2018; Gao et al., 2015). Phthalates [phthalic acid (PA) diesters] also leach into the bottled water after exposure to a high or low pH, temperature and pressure, irradiation [ultraviolet (UV), sunlight, microwaving], or contact with lipid or different solvents (Benjamin et al., 2015). These conditions would accelerate the leaching of phthalate into the environment, as they are not chemically stable in plastics. Ingestion of the phthalates can be harmful to human health, since all cells of human body have the potential for absorption of phthalates, even it can cross placenta, generating the acute toxicity, ecotoxicity, environmental fate, chronic toxicity, and even mutagenicity (Benjamin et al., 2017).

Glass bottles seem to be a better option for packaging and storage of water or other beverages, since the glass is reusable, does not contaminate the content, and is considered more environmentally friendly than plastic polymers. However, if the storage conditions are not proper, it has been demonstrated that, under certain conditions, glass bottles can contaminate water with Pb, Zr, Fe Cr, and Co that are added during the production process, such as dyes (Reimann et al., 2010; Marcussen et al., 2013) more elements leach from glass than from PET bottles (Misund et al., 1999).

In this context, the beverage packaging fields are focusing on the chemical modification of packaging materials and the development of new advanced polymers, which cannot influence the product qualities or the environment, with high performance in the conservation process of beverages like water, beer, wine, juice, and food security (Ramos et al., 2015).

9.2 Biodegradable Polymers

Biodegradable polymers (BDPs) are defined as polymers derivated from renewable resources, especially materials that can be decomposed to simple substances (CO_2, other inorganic compounds, CH_4,

H_2O, biomass), under the microbial enzymatic action (Kržan, 2012). In the United States and the European Union these polymers, along with glass, are the most convenient beverage bottles, due to their properties: softness, lightness, and transparency (Kregiel, 2015).

The BDPs can make significant contributions to material recovery, reduction of landfill, and utilization of renewable resources. Therefore, there is a need to use a renewable, biodegradable, eco-friendly, reusable packaging materials for liquids, thereby avoiding the need for throwing used packaging (http://www.iiprd.com/edible-water-bottlecontainer-technological-perspective, n.d.). According to their production method or the extraction source *BDPs* can be classified as: (1) *polymers extracted from natural (plant) materials*: polysaccharides (starch, cellulose) and proteins (casein, wheat gluten); (2) *polymers produced by chemical synthesis from renewable bio-derived monomers*: An example is polylactate, the biopolyester polymerized from lactic acid monomers; and (3) *polymers produced by microorganisms or genetically transformed bacteria*: polyhydroxy-butyrates and copolymers of hydroxy-butyrate (HB) and hydroxy-valerate (HV), polyhydroxyalkanoates (PHAs), bacterial cellulose, xanthan, and pullan (Gabor and Tita, 2012; Petersen et al., 1999):

9.2.1 Polymers Extracted From Natural (Plant) Materials

A new trend emerging in the bottled water market is bioplastic bottles obtained from plants, as opposed to the mixed composition bottles that were introduced in recent years. In this context, cellulose naturally present in all plants, offers excellent properties like biocompatibility, lower density, substantial strength, and also, inexpensive. In addition, the cellulosic materials can be transformed into cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs) with practical applications in the packaging field (Kumar et al., 2018; van Beilen and Poirier, 2008). Nanocellulose is a nanomaterial extracted from vegetable sources (wood, cotton, natural fibers, and lignocellulosic materials) using enzymatic/chemical/mechanical treatments (Castro et al., 2011), thus obtaining sustainable nanomaterial with potential applications in the food industry.

9.2.2 Polymers Produced by Chemical Synthesis From Renewable Bio-Derived Monomers

An alternative to the synthesis of biopolymers *in planta* is the synthesis of small molecules that can be extracted and used directly or indirectly to synthesize polymers, typically via chemical modification and polymerization. Market studies showed that poly-lactic acid (PLA) is an economically feasible material for packaging, that has been approved by the Food and Drug Administration (FDA) for direct contact with biological fluids (Jimenez et al., 2013). The PLA has unique properties like good appearance, high mechanical strength, low toxicity, permeability performance against transfer of gases, water vapor, and aroma molecules, alone as well as in combination with other polymers as blend or copolymer (Muller et al., 2017; Jamshidian et al., 2010).

9.2.3 Polymers Produced by Microorganisms

The PHAs are linear polyesters that consists of 3-hydroxy fatty acids and are produced naturally by bacterial fermentation, these biogenic polyesters represent a potential sustainable replacement for fossil fuel-based thermoplastics (Bugnicourt et al., 2014). Due to their impermeability to water and air, PHAs are used for the production of bioplastic products such as bottles, films, and fibers. In the industrial production of PHA, the polyester is extracted and purified from the bacteria by microbial fermentation of sugar or glucose. It is estimated that PHA market consumption will grow from an estimated 10,000 MT in 2013 to 34,000 MT by 2018 (Bhatt et al., 2011).

Poly(3-hydroxybutyrate) (PHB) is the best characterized homopolymer of the polyhydroxy-alkanoate family, produced by the bacteria, *Bacillus* spp. being the best producer as a form to store carbon and energy, under different stress conditions (Rizk et al., 2013; Galia, 2010). They are polymers possessing properties similar to various synthetic thermoplastic like PP (Verlinden et al., 2007). Due to these interesting properties (blends with natural additives, mechanical stability), PHB is expected to be a good candidate to substitute PE or PET in beverage applications (Bugnicourt et al., 2014; Getachew and Woldesenbet, 2016).

Compared to the better known poly(hydroxybutyrate) (PHB), the poly(hydroxybutyrate-co-hydroxyvalerate) (PHB-V) has high flexibility, toughness, and has lower melting and glass transition temperatures, depending on PHV contents (Biernacki et al., 2017). Currently, the industrial production of PHB-V is based not only on bacteria like *Escherichia coli* (Lian et al., 2014), but also on yeast like conventional species like *Saccharomyces cerevisia* (Kocharin et al., 2012) and unconventional species like *Kloeckera* spp. (Abd-El-halaem et al., 2007), *Pichia pastoris* (Abd-El-halaem et al., 2007), *Yarrowia lipolytica* (Li et al., 2017), and *Arxula adeninivorans* (Biernacki et al., 2017).

9.3 Plastic Polymers Degrading Microorganisms

Degradation of a polymer may result from the action of microorganisms, macroorganisms, photodegradation, or chemical degradation.

Biodegradation is due to the enzyme-catalyzed hydrolysis and nonenzymatic hydrolysis. Microorganisms like bacteria and fungi showed a chemical degradation of polymers from plastic (David et al., 1994; Chandra and Rustgi, 1998; Mohanty et al., 2000) and considered to be the major mechanism of release of most chemicals into the environment. During degradation, exoenzymes break down complex polymers into oligomers, dimers, and monomers, able to pass the outer bacterial membranes and then able to be utilized as carbon and energy sources (Gu, 2003). This is called depolymerization, involving the degradation and assimilation of polymers by living microorganisms based on their metabolic pathway. The final degradation of a polymer produces organic acids, CO_2, CH_4, and H_2O (Fig. 9.1) (Narayan, 1993).

The biodegradation mechanisms mediated by microorganisms are influenced by two different processes:

(a) The plastic deterioration generates nutritive substance for the growth of the microorganisms (direct action).

(b) The influence of metabolic products on the microorganisms (indirect action) (Mohan, 2011).

Scientifically research have demonstrated that fungal strains like *Phanerochaete chrysosporium*, *Trametes versicolor*, *Streptomyces sp.*, *Aspergillus niger*, *Pleurotus ostentus*, *Geophyllum trabeum*, *Thermonospora*, and *Actinomadura* are capable of degrading polymers like diethylene glycol terephthalate (DTP) and PET (Sharon and Sharon, 2012). One of the most important biological factors involved

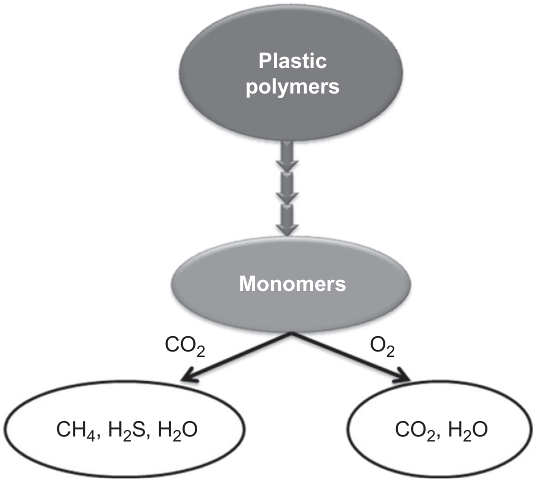

Fig. 9.1 Microbiological degradation of polymeric materials: anaerobic degradation, which results in the production of biogas (as methane and hydrogen); aerobic degradation which results in the production of simple compounds.

in the biodegradation of the plastic polymers are represented by bacteria and fungi. Gram positive (*Streptococcus*, *Staphylococcus*, *Micrococcus*), Gram negative (*Moraxella*, and *Pseudomonas*), and fungal (*Aspergillus glaucus*, *A. niger*) species are involved directly and indirectly in the discoloration and deterioration of plastic polymers and it is the safest method of breakdown which are anticipated to produce less toxic by-products and have the potential for biogeochemical cycling of the substrate (Pramila et al., 2012; Chee et al., 2010). The biodegradation process can occur under aerobic or anaerobic conditions; aerobic microorganisms cut organic compounds into smaller organic components, producing CO_2 and water as the final product. Under anaerobic conditions anaerobic biodegradation occurs when the microorganisms cut organic chemicals into smaller compounds (Mohan and Srivastava, 2010).

The most relevant bacterial species involved in the biodegradation of plastic polymers are *Bacillus* sp., *Pseudomonas* sp., *Klebsiella* sp., *Actinomycetes* sp., *Nocardia* sp., *Micromonospora* sp., *Mycobacterium* sp., *Flavobacterium* sp., *Comamonas* sp., *Escherichia* sp., and *Azotobacter* sp. (Sangale et al., 2012). The fungal species actively participating in the biodegradation process are *Sporotrichum* sp., *Talaromyces* sp., *Phanerochaete* sp., *Ganoderma* sp., *Thermoascus* sp., *Thielavia* sp., *Paecilomyces* sp., *Thermomyces* sp., *Geotrichum* sp., *Cladosporium* sp., *Phlebia* sp., *Trametes* sp., *Candida* sp., *Penicillium* sp., *Chaetomium* sp., and *Aerobasidium* sp.

9.4 Biodegradation of Synthetic Polymers From Water and Beverages Packaging

It has been demonstrated that biodegradation of poly(vinyl) alcohol (PVA) extends back 70 years since the first study reported the microorganism involved in this process to be Fusarium lini (Fusako and Hu, 2009; Kim and Rhee, 2003). Isolated strains belonging to the genus *Pseudomonas* from soil have been growing on PVA as the source of carbon, which are suitable for biodegradation due to polivinyl alcohol dehydrogenase (PVADH) which degrades the PVA (Leja and Lewandowicz, 2010).

Also, fungal species such as *Phanerochaete chrysosporium*, *Lentinus tigrinus*, *A. niger*, and *A. sydowii* are have been shown to be able to degrade effectively PVC (Ali, 2011; Ali et al., 2013).

Poly(ε-caprolactone) (PCL) can be degraded by numerous species of bacteria largely distributed in nature (Nishida and Tokiwa, 1993; Suyama et al., 1998), for example, several species of filamentous fungi and yeasts are able to hydrolyze PCL. It has been demonstrated that esterases and lipases are able to hydrolyze PCL

(Tokiwa and Suzuki, 1977b). It has been reported that synthetic polyesters such as PCL, poly(ethylene dicarboxylic acids), and poly(butylene dicarboxylic acids) can be degraded by lipases from *Rhizopus delemar* (Tokiwa and Suzuki, 1977b) and *Rhizopus arrhizus* (Tokiwa et al., 1986). It has been shown that PCL was degraded under anaerobic condition by *Clostridium* sp. strains (Abou-Zeid et al., 2001). Other PCL degraded fungi are *Aspergillus*, *Aureobasidium*, *Chaetomium*, *Cryptococcus*, *Penicillium*, and *Thermoascus* (Leja and Lewandowicz, 2010).

There have been reports that a mutant of *F. solani* was able to degrade PCL and cutin, while the wild-type strains of Fusarium sp. commonly hydrolyzed both polyesters (Murphy et al., 1996). The production of PCL depolymerase in the wild-type strain was induced by addition of the cutinase inducer, 16-hydroxyhexadecanoic acid. There have been reports of several poly(β-propiolactone) (PPL)-degrading microorganisms widely distributed in different environments, and majority of these microorganisms belong to Bacillus sp., *Acidovorax* sp., *Variovorax paradoxus*, *Sphingomonas paucimobilis*, *R. delemar* and *Streptomyces sp.* (Leja and Lewandowicz, 2010).

Bacterial species involved in the biodegradation of polybutylene succinate (PBS) and polyethylene succinate (PES) are *Amycolatopsis* sp., *Microbispora rosea*, *Excellospora japonica*, and *Excellospora viridilutea* (were able to degradate PBS) (Jarerat and Tokiwa, 2001a,b). From the soil a thermophilic *Bacillus* sp. TT96, a PES degrader, has been isolated (Leja and Lewandowicz, 2010). Also fungi belonging to *A. clavatus*, *R. delemar* (Bikiaris et al., 2006) have been revealed as PES biodegradators. Aliphatic polyesters [PEA, PES, polypropylene adipate (PPA), PBA, PBS, and polyhexylene] can be hydrolyzed by several filamentous fungi such as *Aspergillus flavus*, *A. niger*, *A. versicolor*, *Aureobasidium pullulans*, *P. funiculosum*, and *Chaetomium globosum* (Kim and Rhee, 2003).

It has been demonstrated that aliphatic-aromatic copolyester (AAC) was hydrolyzed by *R. delemar* lipase, hydrolase and esters from *Thermobifida fusca* (Kleeberg et al., 1998).

Different aerobic and anaerobic poly(3-hydroxybutyrate) (PHB)-degrading microorganisms have been reported, for example, *Pseudomonas lemoigne, Comamonas sp., Acidovorax faecalis*, *A. fumigatus*, and *V. paradoxus in soil, Alcaligenes faecalis, Pseudomonas, Ilyobacter delafieldi* in anaerobic sludge, and *Comamonas testosterone*, *Pseudomonas stutzeri* in seawaters and lakewaters (Lee, 1996). The PHB are degraded by several fungi genera, for example, *Acremonium* sp., *Cladosporium* sp., *Debaryomyces* sp., *Emericellopsis* sp., *Eupenicillium* sp., *Fusarium* sp., *Mucor* sp., *Paecilomyces* sp., *Penicillium* sp., *Pullularia* sp., *Rhodosporidium* sp., and *Verticillium* sp. (Leja and Lewandowicz, 2010).

PLA can be degraded by lipase from *R. delemar* and the proteinase K from *Tritirachium album* (Leja and Lewandowicz, 2010). It has been demonstrated that PLA can also be hydrolyzed by PU depolymerase from *Comamonas acidovorans* (Akutsu et al., 1998). It has been proved that PLA is highly resistant to microbial attack in the environment (Suyama et al., 1998). The most common environmental biodegradators of PLA are represented by the genus *Amycolatopsis* from *Actinomycetes* (Leja and Lewandowicz, 2010) and by filamentous fungi *Penicillium roqueforti* and *Tritirachium album* (Nakamura et al., 2001).

Thermomonospora fusca and *Streptomyces albus* were able to degrade polyesters (Mueller, 2006) but there have been reports that the molecular mass and crystallinity reduced the biodegradability (Nishida and Tokiwa, 1993).

Fungi and bacteria are involved in the biodegradation of the nylons, for example, *Geobacillus thermocatenulatusis* was used to biodegrade nylon 12 and nylon 66 (Tomita et al., 2003). It has been shown that bacterial degradation of nylon 12 was associated with the enzymatic hydrolysis of amine bonds, accompanied by the formation of 12-amino dodecanoic acid.

In the biodegradation of the PE fungi species are involved due degrading enzymes (Volke-Sepulveda et al., 2002) and polysaccharides, which are used to colonize the polymer surface and also for the distribution and spreading of the mycelium (Manzur et al., 2004). Fungal isolates can be used for studying PE biodeterioration, for example, *Phanerochaete chrysosporium* (Orhan and Buyukgungor, 2000), *A. niger* (Volke-Sepulveda et al., 2002), and other species like *A. terreus*, *A. fumigatus*, *A. flavus* (Zahra et al., 2010). It has been demonstrated that bacterial rods are able to degrade PE, for example, *Rhodococcus ruber* (Sivan et al., 2006), *Brevibacillus borstelensis*, and several species of *Bacillus* (Abrusci et al., 2011).

Polyethylene adipate (PEA) a prepolymer of PU was degraded due to a lipase with broad substrate specificity from microorganisms belonging to *Penicillium* sp. It has been shown that PEA and PLA can be degraded by *R. arrhizus*, *R. delemar*, *Achromobacter* sp., and *Candida cylindracea* (Tokiwa and Suzuki, 1977a,b).

Plastic can be degraded by strains of *Pseudomonas* sp. (e.g., polythene, PVC, PHB). Polycaprolactone is degraded by strains belonging to *Bacillus brevis* and PHB by *Streptomyces* sp. It has been demonstrated that *Ochrobactrum* TD was also able to degrade PVC (Leja and Lewandowicz, 2010). There have also been reports about other bacterial species with the properties of degrading plastics belonging to Gram positive and Gram negative rods (Kathiresan, 2003).

9.5 Nanoparticles as Promotors for Biodegradation

It has been shown that nanoparticles of nano barium titanate, fullerene 60, and iron oxide are able to degrade PE thanks also to the intervention of microbial consortium activity consisting of *Microbacterium* sp., *Pseudomonas putida*, and *Bacterium* Te68R (Kapri et al., 2010).

9.6 Conclusions

Over the last 10 years more plastic has been produced than during the whole of the last century, 40% of the total plastic wastes of average American family are being provided by the use of plastic bottles. According to the *Environmental Protection Agency* (EPA), 29 million tons of plastic wastes were discarded in 2012 from residential, commercial, and institutional sources. A new approach to beverage packaging is based on the providing environmentally friendly solutions in order to develop BDPs from renewable resources.

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CONTRIBUTION OF MINERAL AND TAP WATER TO THE DIETARY INTAKE OF AS, B, CA, CE, CU, F, LA, LI, MO, NI, P, PB, SR, U, AND ZN BY HUMANS

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10.1 Introduction

In the past it was bread, nowadays water is number one food in the significance listing of the human diet. This is for good reason as water is essential for all organisms as biochemical reactions take place entirely in aqueous media. Water is the universal transport medium for nutrients and it regulates the temperature of endotherm organisms (Hendel and Ferreira, 2001). Water is the most common beverage, either on its own, or in mixed drinks. In Table 10.1 the annual amount of water consumed directly and with other beverages in Germany are listed. On an average a person consumes 2 L of water per day, most of it immanent in beverages (Table 10.1; Quattrini et al., 2016).

In this chapter German law is exemplarily cited and all information refers to the German version of the relevant ordinances. German law differentiates between mineral, spring, curative, table, and tap (potable) water and regulates its chemical and microbiological composition, and production. Potable water is regulated by the tap water ordinance (Trinkw, 2006), mineral, spring, and table water in the Mineral and

Bottled and Packaged Water. https://doi.org/10.1016/B978-0-12-815272-0.00010-6

Table 10.1 Annual Consumption of Beverages in Germany

Beverage	Annual Consumption Per Capita (L)	Quota of Natural Water (L)
Alcohol	146	116
Beer	116	116
Wine	20.1	
Sparkling wine	3.80	
Spirits	5.70	
Non alcoholics	297	238
Bottled waters	140	140
Soft drinks[a]	117	76.4
Juices[b]	39.8	21.8
Hot and home drinks	313	219
Coffee	148	148
Tea	70.9	70.9
Milk	91.3	
Tap water	183	183
Total amount of liquids	938	758
Daily amount of liquids	2.49	2.08

[a] 40.7 L of soft drinks are definitively made from de-ionized water.
[b] 18.0 L fresh or direct squeezed juices; references: Websites and publications (2008–2010) from Unions of the Beverage Industries, the Federal Statistical Office, the Federal Agency for Agriculture, and Food and Schulz et al. (2008).

Table Water Ordinance (MTVO, 2006). Curative waters are considered as drugs and therefore covered by the German Pharmaceuticals Act (AMG, 2013). Within the European Union (EU) the water ordinances of the individual member states are harmonized by the Directive 98/48/EC of the European Parliament and of the Council of July 20, 1998 (Anonymous, 2017).

In Germany, mineral waters are regulated by the Mineral and Table Water Ordinance (MTVO, 2006). Mineral waters must originate from a natural, unpolluted subterranean aquifer. It is collected at the spring naturally or technically. All relevant characteristics of the water such as composition and temperature need to be constant within the typical variability of the natural background (MTVO, 2006). The official approval of a mineral water comprises >200 parameters, some of which have to be analyzed on a daily basis.

Like mineral water, spring water derives from natural subterranean pristine sources and is legally covered by the Mineral and Table Water

Ordinance (MTVO, 2006). The main difference between mineral water and spring water is that the quality of spring waters need not be proven. Fe, Mn, and S can be removed by means of aeration, decantation, and filtration. Carbon dioxide may be added or removed if the typical chemical composition of the spring water is not changed.

By definition curative waters are natural ground waters with special chemical composition (e.g., trace elements) or physical features (e.g., temperature), which bear balneologic or medical features of therapeutical value. Curative waters must have a total dissolved solid (TDS) content of at least 1000 mg/L. In Germany and Austria the appellation curative water requires a formal approval.

Table water is by law an artificial mineral water, which may contain additives to improve its palatability (MTVO, 2006). Declarations of geographical origin or chemical composition are not permitted.

Tap water in Germany is regulated by the tap water ordinance (Trinkw, 2006; Heinrich, 2006). It is defined as fresh water with a high level of purity and is retained from very different sources such as natural precipitation, lakes, reservoirs, ground, and spring water (Donhauser and Riese, 2009).

The main difference between the different legally defined waters is their mineral content: general and tap waters show the lowest and curative waters show the highest concentrations (Schnug et al., 2018; Petraccia et al., 2006). In this chapter the term mineral water is used synonymously with bottled waters of natural origin, without differentiating between legal classes.

Bottled mineral waters enjoy an ever-increasing popularity, not only for quenching one's thirst but also as a lifestyle hallmark without being related to material or health aspects (Pils, 2010). Even in countries where fresh water was for free on every table not so long ago, nowadays bottled water needs to be purchased with the meals (Fig. 10.1).

In some regions the price for bottled water is even higher than alcoholic beverages (Toerne, 2002). There is a stiff competition within the market for bottled waters to give a faceless commodity its own identity: for instance, mineral waters were declared to be superior to drinking water. One brand, Extaler, claims that the water is “the stuff drunk by our heroes for health and strength” as it is rich in Ca (Anonymous, 2018). Beneficial attributes of minerals such as Ca and F in bottled water are regulalry used for promoting development and health of teeth.

In contrast to being potentially health supporting, mineral waters are consistently suspected as a source of toxic contaminants, for instance, As and U. So Chandrajith et al. (2010) associate the increasing number of chronic kidney disease (CKD) patients without identifiable cause (CKD of uncertain etiology) with an increased exposure to U for which Schnug and Lindemann (2006) surmise mineral waters as a potential source.

Fig. 10.1 Free water for everyone in the roads of Cairo *(left)* and in a restaurant in Delhi *(right)*. Photos: Ewald Schnug (2004, 2013).

From a physiological point of view minerals in drinking water can be beneficial and toxic for humans depending on their concentration. It was Paracelsus (1538) who claimed "... only the dose determines if a substance is poisonous or not." In Fig. 10.2 the relative element-specific toxicity for humans is reflected considering occupational limits as limit values for drinking water that exist only sporadically.

U has been assigned a value of 0.25 mg/m^3 as the occupational limit in Fig. 10.2. The recommended exposure limit (REL) and permissible exposure limit (PEL) for U dust is 0.05 mg/m^3 according to National Institute for Occupational Safety and Health/Occupational Safety and Health Administration (NIOSH/OSHA). The Nuclear Regulatory Commission (NRC) reports an occupational limit of 0.2 mg/m^3 for U (ATSDR, 1999). The value of 0.25 mg/m^3 for U in Fig. 10.2 addresses the chemical toxicity exclusively while the radiological or combined chemical/radiological toxicity through secondary photon emission damage has been neglected (Busby and Schnug, 2008).

It is the objective of the present chapter to evaluate the intake of elements by water which are known to be toxic to humans such as Cr, Cd, As, Pb, Ni, and U, essential nutrients like B, Ca, and P, and the intermediates Cu, F, Mo, and Zn which may unfold positive and detrimental effects. Last but not least proposed beneficial elements such as Ce, La, Li, and Sr have been considered. Relevant in the context of human toxicology is that it is not sufficient to have data on elemental concentrations in water, but its contribution to the overall dietary mineral balance is also essential. Moreover, this implies that the intake of minerals by water must be distinguished from that by solid food.

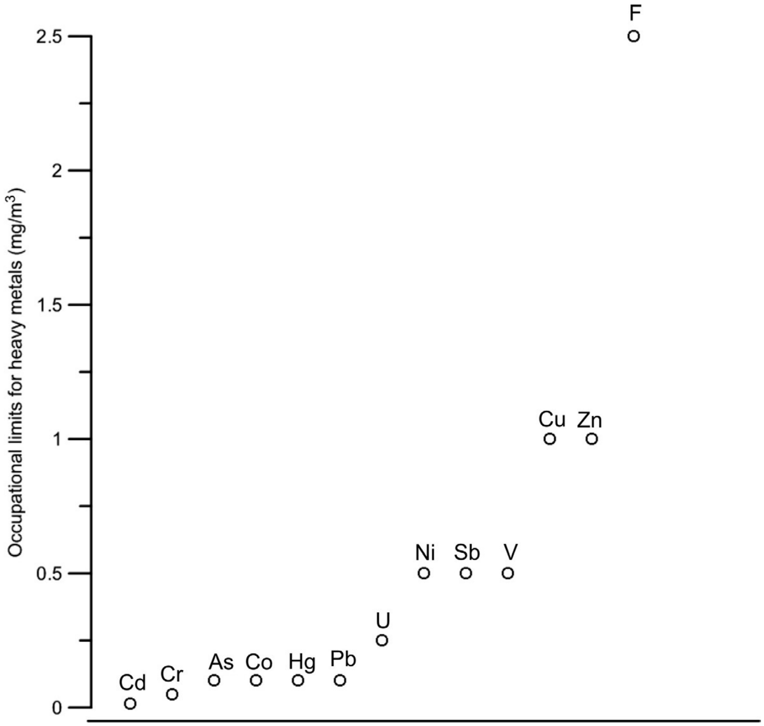

Fig. 10.2 Relative element-specific human toxicity of selected minerals.

10.2 Methodology for Assessing the Contribution of Mineral Waters to the Diet-Related Mineral in Take of Humans

To evaluate the relative significance of water to the total daily intake of minerals requires detailed information about consumption and composition of solid foods. EFSA (2009) provides the so-called *Concise European Food Consumption Database* which comprises food consumption data based on reports of the individual member states of the EU. However, these data show a very high inexplicable variability, which hampers a bias-free comparison of individual diet strategies or drinking habits. EFSA (2009) identified different methodologies employed country wise for data collection and broadly based food categories as the main reasons for distortions in the database. This resulted in bizarre consumption patterns in different countries. So a Dane would consume nearly six times more liquids than a Bulgarian citizen.

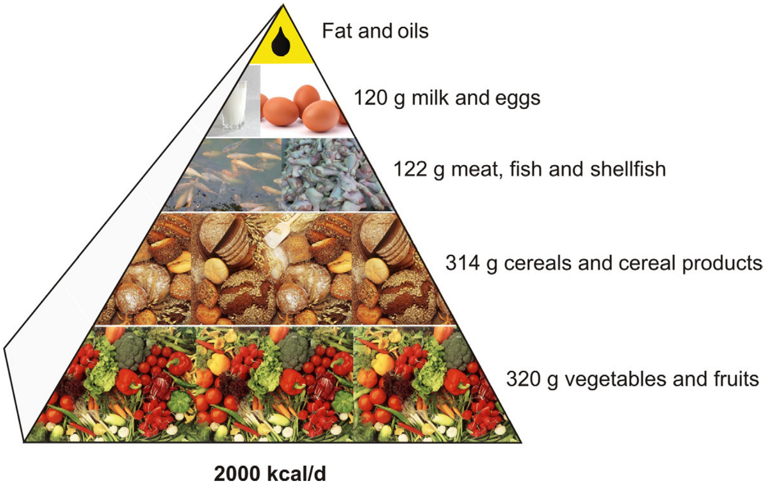

Fig. 10.3 Balanced diet based on the principle of the trophic pyramid providing 2000 kcal/day.

Hassoun (2012) developed a model in which the considerably variable food sources of human diets were assembled in affiliated categories in order to achieve a low bias from mineral intake by solid food. Her standardized healthy diet is based on an energy requirement of 2000 kcal/day (Eastwood, 2003) and follows the rules of the trophic pyramid (Fig. 10.3). This implies that 55% of the total energy demand is provided by carbohydrates, 15% by proteins (5% by milk and milk products and 10% by meat, fish and shellfish and meat, fish, and shellfish products), and 30% by fat (15% from milk and milk products and 15% from meat, fish and shellfish and meat, fish, and shellfish products). This equals a daily diet of 314 g cereals and cereal products, 122 g meat/fish/shellfish and their products [(meat:fish = 6:1) includes 2% offal], 120 g milk/egg and their products, 320 g vegetables and fruits (of which 44% leaf vegetables, 38% root vegetables, and 18% fruits). Henceforth the categories will be referred to in short form as cereals and cereal products, meat, fish and shellfish, milk and eggs, and vegetables and fruits to make text, tables, and figures easier to read.

The underlying mean energy content of these food categories are: 350 kcal/100 g for cereals and cereal products, 100 kcal/100 g for fish and shellfish (10% fat), 250 kcal/100 g for meat and meat products including offal and their by-products with 20% fat (at a ratio of meat:fish of 6:1 the average energy content of this source would be 228 kcal/100 g), 250 kcal/100 g for milk and eggs (20% fat), and 60 kcal/100 g for vegetables and fruits.

In a next step Hassoun (2012) diversified the standard diet into three additional dietary styles: ovo-lacto vegetarian, vegan, and carnivore. The relative energy input from the different food categories defined above to the total of 2000 kcal/day in relation to dietary style is illustrated in Table 10.2.

Table 10.2 Relative Contribution of Different Food Categories to the Energy Input of 2000 kcal/day in Relation to Dietary Style and Mean Consumption (g/day) of Food From Different Categories in Order to Maintain an Energy Input of 2000 kcal/day (Hassoun, 2012)

Dietary Style	Cereals and Cereal Products	Meat, Fish, and Shellfish	Milk and Eggs	Vegetables and Fruits
Energy input (%) from food category				
Standard	55	14	15	16
Vegetarian (ovo-lacto)	50	0	25	25
Vegan	60	0	0	40
Carnivore	30	50	10	10
Daily consumption (g/day) from food category				
Standard	314	123	120	320
Vegetarian (ovo-lacto)	200	0	200	833
Vegan	343	0	0	1333
Carnivore	171	439	80	333

10.2.1 Mineral Concentrations in Solid Food

A meta-data analysis consisting of >1000 entries was carried out in order to assess the mean concentrations of As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn in different food categories (Hassoun, 2012; Holzhausen, 2016). The mean concentrations are listed in Table 10.3.

Based on the data provided in Table 10.3 the highest concentrations of As, Ce, Cu, U, and Zn were found in food from the category meat, fish, and shellfish, that of Li and Ni in the category cereals and cereal products, and that of B, F, Mo, P, and Pb in the category vegetables and fruits. The category milk and eggs showed the highest concentrations of Ca, La, and P. The lowest As, B, Ce, Cu, Li, Mo, Ni, Pb, and U concentrations occur in milk and eggs, and the lowest Ca, F, La, P, and Sr concentrations in the category cereals and cereal products (Table 10.3).

Table 10.3 Mean Concentrations (mg/kg) of As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn in Different Food

Element	Cereals and Cereal Products	Meat, Fish, and Shellfish	Milk and Eggs	Vegetables and Fruits
As	0.09	3.32	0.01	0.03
B	3.5	0.63	0.43	5.06
Ca	449	556	9288	3774
Ce	0.436	3.57	0.593	3.08
Cu	1.92	11.3	0.69	1.95
F	1.06	2.26	1.70	4.44
La	0.597	2.99	4.34	1.84
Li	0.21	0.07	0.07	0.1
Mo	0.41	0.38	0.14	0.46
Ni	0.38	0.18	0.05	0.37
P	3153	5663	7944	3697
Pb	0.07	0.11	0.03	0.15
Sr	14.6	17.2	34.0	83.6
U	0.002	0.002	0.001	0.001
Zn	15.5	25.7	10.5	5.67

Data from Hassoun, R., 2012. Eine statistische Auswertung des Beitrages von Mineral - und Leitungswasser zur Aufnahme von As, B, Cu, Li, Mo, U und Zink in der menschlichen Ernährung. PhD Thesis, Braunschweig. https://publikationsserver.tu-braunschweig.de/receive/dbbs_mods_00042027 (Accessed 24 January 2018) and Holzhausen K., 2016. Zum Beitrag von Mineral- und Leitungswässern zur entwicklungsphasenabhängigen Aufnahme zahnbildender Mineralstoffe (Calcium, Phosphor, Fluor, Strontium und ausgewählten Seltenen Erden wie Lanthan und Cer) mit der Nahrung. PhD Thesis, Braunschweig. https://publikationsserver.tu-braunschweig.de/servlets/MCRFileNodeServlet/digibib_derivate_00041864/Diss_Holzhausen_Kristin.pdf (Accessed 24 January 2018).

10.2.2 Mineral Concentrations in Bottled Mineral and Tap Water

Knolle et al. (2008, 2009), Smidt (2012), Hassoun (2012), and Holzhausen (2016) established a database with elemental data for 3297 bottled mineral waters worldwide and 637 data sets for German tap water. The complete analytical data and descriptive statistics are provided by Schnug et al. (2018). In Table 10.4 the mean concentrations of As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn in bottled mineral and tap waters are provided.

The results summarized in Table 10.4 showed that the highest mean concentrations of all elements can be found in the group mineral waters of the world and the lowest in German tap water with the exception of Cu, Pb, and Zn which were found in highest mean concentrations in

Table 10.4 Mean As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn Concentrations in Bottled Mineral and Tap Waters (Hassoun, 2012; Holzhausen, 2016)

		Mineral Water				**Tap Water**
		Mineralization Degree		**World**	**Germany**	**Germany**
		Low	**High**			
Element	**Unit**	**<50 mg/L**	**>1000 mg/L**	***n*=3297**	***n*=637**	***n*=621**
As	µg/L	3.03	23.4	6.52	1.92	1.27
B	µg/L	55.2	1719	672	227	40.7
Ca	mg/L	12.1	362	78.3	149	66.3
Ce	µg/L	0.066	0.027	0.028	0.012	0.075
Cu	µg/L	0.18	0.03	6.24	3.45	78.8
F	µg/L	448	674	509	391	111
La	µg/L	0.078	0.014	0.029	0.022	0.006
Li	µg/L	5.01	10.5	328	910	20.3
Mo	µg/L	17.4	1060	1.29	0.69	0.32
Ni	µg/L	0.7	3.24	4.10	3.69	3.74
P	µg/L	53.1	61.7	50.8	61.8	83.3
Pb	µg/L	3.9	7.13	0.91	0.69	1.07
Sr	µg/L	129	5394	991	2404	301
U	µg/L	0.95	0.86	3.54	3.08	1.67
Zn	µg/L	1.45	7.54	14.4	0.73	151

German tap water. This indicates strongly an anthropogenic influence through contamination from installation materials.

Mineral waters are best differentiated by their mineralization degree expressed by the contents of TDSs, which is closely related to their total elemental concentration (Table 10.4).

Based on the data presented in Table 10.4 the highest mean concentrations for different elements are usually found in mineral waters with a high mineralization degree (TDS > 1000 mg/L). In the case of Cu the concentrations were higher in low mineralized mineral waters. The higher Cu concentrations in waters with low mineralization degree suggest that these might be not pure well waters as stipulated in the Mineral and Table Water Ordinance (MTVO, 2006), but mixtures of mineral and tap water. The U concentrations seem to be affected only minor by the mineralization degree (Table 10.4).

10.3 Significance of As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn for Human Health and Contribution of the Mineral and Tap Water to the Dietary Intake by Humans

The following tables will present brief information on the significance of each element treated in this section for human health followed by mean exposure estimates for different dietary styles and water consumer types. It should be mentioned here that throughout this section the question of bioavailability of the elements is neglected and just the entire elemental balance has been evaluated. Reason for this is the tremendous inconsistency of absorption rates depending on the matrix in which the element is administered and on the conditions of the organism itself (Bohmer et al., 2000; Burckhardt, 2008; Dumartheray et al., 2006; Waldvogel et al., 2002).

10.3.1 Arsenic (As)

Arsenic (As) is a metalloid and highly toxic to humans (Dartmouth Toxic Metal Research, 2001). It is classified as the most poisonous of the 20 most hazardous substances (Goering et al., 1999). Organic As compounds are less dangerous than the inorganic forms (RAIS, 2005), but it is the last one which is of significance in mineral and tap waters.

In the 19th century As compounds were used in human medicine to treat certain skin diseases, syphilis, and digestive problems. Later it has been noticed that some of these drugs could develop cancer at the skin sites where the drug was applied. Between the 1940s and 1950s most medical products containing As were suspended. However, some As containing pharmaceuticals are still prescribed, for instance, Melarsoprol against sleeping sickness in Africa (Dartmouth Toxic Metal Research, 2001; Roy and Saha, 2002).

Because of its low As content, food is not a major concern for As poisoning (Table 10.5). As is present in extremely small concentrations in milk, vegetables, and fruits. As concentrations in fish and shellfish are distinctly higher (Dartmouth Toxic Metal Research, 2001, Table 10.5). The presence of As in drinking water is of more concern for human health than in foods. The US Environmental Protection Agency (EPA) has determined a limit value of 0.01 mg/L for As in drinking water (ATSDR, 2007a). Several epidemiological studies have shown that As concentrations in drinking water can increase the risk of skin, liver, and bladder cancer as well as of respiratory and gastrointestinal tracts (RAIS, 2005). Exposure to As in drinking water has become a health concern in the United States because of a high As content in bedrocks (Dartmouth Toxic Metal Research, 2001). Exposure to As are classified

Table 10.5 Mean As, B, and Ca Exposure Estimates for Different Water Consumer Types in Different Dietary Group Scenarios

Scenario	Abbreviation	As (μg/day)	B (μg/day)	Ca (mg/day)
Consumed water type				
Tap water	1 TW	2.54	81.4	133
German bottled mineral water	2 GBW	3.84	454	298
World bottled mineral water	3 WBW	13.0	1344	157
Low mineralized bottled water	4 LMBW	6.06	110	24.2
Highly mineralized bottled water	5 HMBW	46.8	3438	724
Dietary style				
Standard	I	447	2847	2532
Vegetarian, ovo-lacto	II	45.0	5001	5091
Vegan	III	70.9	7946	5185
Carnivore	IV	1484	2594	2321
Daily intake				
Minimum daily intake (water type + dietary style)		1 + II	1 + IV	4 + IV
Minimum daily intake (μg/day)	A	47.54	2675	2345
Minimum daily intake scenario: contribution of water (%) to daily intake		5.3	3.0	1.03
Maximum daily intake scenario: water type + dietary style		5 + IV	5 + III	5 + III
Maximum daily intake (μg/day)	B	1531	11,384	5909
Maximum daily intake scenario: contribution of water (%) to daily intake		3.1	30.2	12.3
Personal Intake Strategy	**Formula**			
Maximum reduction potential (%) of daily intake	(A/B*100) − 100	−97	−77	−60
Maximum increase potential (%) of daily intake	(B/A*100) − 100	+3120	+326	+152

into two: acute and chronic exposures. Acute exposure to a high dose in a short period of time yields immediate effects, while chronic exposure to a lower dose of As over a longer period of time produces gradually delayed effects (Dartmouth Toxic Metal Research, 2001). Acute exposure to inorganic As causes nausea, anorexia, vomiting, abdominal pain, and diarrhea (RAIS, 2005). Ingestion of low doses of inorganic As over a long period of time can cause small warts on the sole and palms and a darkening of the skin (ATSDR, 2007a). Many studies have reported a relationship between ingestion of inorganic As and increase of the risk of skin, lung, liver, kidney, bladder, and prostate cancer (RAIS, 2005; ATSDR, 2007a).

An ovo-lacto vegetarian diet supplies the smallest daily amount of As with 45 μg/day by solid food to the human body while a meat-rich dietary style delivers 33 times higher intake (Table 10.5). The highest As concentrations were found in highly mineralized bottled water.

The contribution of water to the daily As intake of a standard diet consumer drinking tap water is 0.57%. An ovo-lacto vegetarian diet reduces the As intake by a factor of 10 compared to the standard diet. If this dietary style is combined with the consumption of tap water the consumer yields the maximum reduction potential of 97% of his daily As intake. In comparison, a meat-rich diet combined with the consumption of highly mineralized bottled water delivers the highest value for the daily As intake with 1531 μg/day (Table 10.5).

10.3.2 Boron (B)

Boron (B) is a trace element essential for all living systems. It occurs mostly in the form of inorganic borates, salts of the boric acid. Most of the borates and boric acid are absorbed from the gastrointestinal and respiratory tracts and rapidly excreted in the urine from the human body (Green Facts, 2004). This is the reason why B does not accumulate in organisms. Regarding B effects on human health, several animal studies indicated that ingestion of large amounts (1800 times the average daily intake) affect male reproductive organs, mainly the testis and interfere with the development of the fetus (ATSDR, 2007c). Acute exposures to high levels of B (30 g of boric acid) damage stomach, liver, kidney, intestines, testis, and brain, and may also lead to death. Short-term exposure to high doses of B causes reversible nose, throat, and eyes irritation (ATSDR, 2007c; Green Facts, 2004). B has been classified as being not carcinogenic to humans (ATSDR, 2007c). As anthropogenic activities constantly increase B loads to the aquatic environment, mainly through B containing household chemicals (detergents), all drinking water resources face the risk of increasing B concentrations in future.

Among solid foods plant materials provide the highest amounts of B (Table 10.5). A carnivore diet supplies the smallest amount of B with solid food to the human body (2594 μg/day) whereas a vegan diet delivers three times more B (Table 10.5). A tap water consumer will have the lowest (81.4 μg/day) and a consumer of highly mineralized bottled water has the highest daily B intake (3438 μg/day) with water (Table 10.5).

The contribution of drinking water to the daily B intake of a standard diet consumer drinking tap water is 2.8%. This value is as high as 57% for a highly mineralized bottled water consuming carnivore and 1.6% for a tap water consuming vegetarian (Table 10.5). The maximum reduction potential for the daily B intake through a change of water drinking and dieting habits is −77% (Table 10.5).

10.3.3 Calcium (Ca)

Calcium (Ca) is the most abundant mineral in the human body. Ca accounts for 39% of the mineral inventory of a body whereby the majority of the Ca is allocated to bones, teeth, and plasma (Biesalski et al., 2002; Quattrini et al., 2016). Ca in teeth is irreversibly bound, whereas Ca in bones can be remobilized and is therefore a reserve depot for Ca necessary to maintain a constant Ca level in the serum (Stegemann and Davis, 2007). Ca in bones gives a body structural strength and stability; Ca in the blood serum maintains blood coagulation, muscle contractions, transfer of nervous signals, and enzyme activation (Woehrl, 2008). Human bones gain their peak bone density at the age of 30, thereafter it continuously decreases by approximately 1% per year despite a sufficient Ca supply (Hahn, 2011). Ca excretion increases with age causing demineralization of bones (Biesalski et al., 2002).

Mineral waters are supposed to be a preferable source of Ca supply due to the presence of bicarbonate. Ca in water is better absorbed by the organism than from milk and milk products (Baran et al., 1990; Petraccia et al., 2006). According to USDA (1998), Scholz-Ahrens (2003), and many other sources in the international literature >50% of juveniles have a sufficient Ca intake to their bodies. Symptoms of Ca deficiency in humans are acromyotonia, and respiratory difficulties (Stegemann and Davis, 2007). Long-term Ca depletion increases the risk for osteoporosis (Dusso et al., 2005). In contrast, a Ca oversupply is linked to dizziness, flushed facial skin, prickling, constipation, nephrolithiasis, xerostomia, cardiovascular disorders, fatigue, and hypertension (Bolland et al., 2010; Peters et al., 2001).

The highest Ca concentrations in solid foods are found in milk and eggs in a vegetarian diet (Table 10.5), the lowest Ca concentrations occur in cereals and cereal products (Table 10.5). Ca in cereals is physiologically problematic as it is mainly bound insolubly to phytic acid and thus is not available for biological processes (Hahn, 2011).

Ca is one of the elements contributing strongest to the amount of total dissolved substances (TDSs) in water. Consequently, highly mineralized waters show 30 times higher Ca concentrations than low mineralized ones (Table 10.5).

A carnivore-type consumer has the lowest Ca intake with solid foods, only about half of that of a vegetarian and vegan dieter (Table 10.5). The Ca intake can be improved substantially if highly mineralized bottled water is consumed. In all scenarios calculated in Table 10.5 the daily Ca intake is well above the recommended value of 1000 mg/day Ca (NVS, 2008).

10.3.4 Cerium (Ce) and Lanthanum (La)

The lanthanides or rare-earth elements (REEs) comprise the elements Sc (Z = 21) and Y (Z = 39), and 14 lanthanides with successive atomic numbers (Z) from 57 to 71. There is a demarcation between light (La, Ce, Pr, Nd, Sm, and Eu) and heavy (Gd, Th, Dy, Ho, Er, Tm, Yb, and Lu) REEs. Promethium belongs chemically to the group of lanthanides, however, is an artificial radioactive element that is not found in nature. REEs are often used synonymously while Y and Sc are treated separately. The reason is that Sc shows a distinctly different geochemical behavior, and Y mimics heavy REEs (Nozaki, 2001).

Lanthanides show similar physicochemical characteristics. The reason is the identical configuration of valence electrons in their outermost shell, and 4f orbitals are filled up with increasing atomic number while the ionic radius decreases (Zawisza et al., 2011). The latter phenomenon is called lanthanide contraction. This occurrence comes along with decreasing basicity and increasing solubility (Haley, 1991). The chemistry, toxicity, and behavior of lanthanides in environmental compartments are regularly discussed as a group because of their analogy. The ionic radius of lanthanides is comparable to that of Ca so it is widely assumed that their functions and behavior are comparable (Evans, 1990). The elements Ce and La have been chosen as examples for the entire group of REEs. Despite the term rare they are quite common in the mineral world. Ce is for instance more abundant than As, Pb, and Hg (Hollemann and Wiberg, 2016).

Redling (2006), Fricker (2006), and Thompson and Orvig (2006) provided a comprehensive summary of relevant literature on the use for medical applications and health effects of lanthanides, so at this point the main findings are only briefly addressed. China is home to the world's largest REE resources and research in all kinds of use for REEs including nutrition and pharmacology (Hu et al., 2006). Because of chemical similarities REEs interfere in biological systems antagonistically with Ca (Barry and Meehan, 2000; Evans, 1990) and their accumulation in tumor tissue is suspected to cause an anticarcinogenic effect (Dai et al., 2002; Evans, 1990; Weiss et al., 2001; Xiao et al., 1997).

The phosphate-binding capacity and substitution of Ca make REEs predestined for use in renal diseases such as hyperphosphatemia in order to regulate the phosphate level; Ce-nitrate has been successfully used for treating burns (Redling, 2006). The efficacy has been attributed to the direct interaction with the burn toxin and immunosuppressive factors, or alternatively direct binding of Ce to lipid protein complexes (Redling, 2006).

When lanthanides were first used as anticancer agents high doses were required to be administered which gave rise to toxic effects (Kostova, 2005). Kostova (2005) described that the challenges of developing effective lanthanide-based anticarcinogenics is to modulate duality and diversity of single lanthanides. The toxicity of REEs (LD_{50}) is about 10–100 mg/kg body weight (Evans, 1990; Richter, 2003) and goes along with symptoms of acute poisoning like drop of blood pressure (Graca et al., 1964), loss of appetite, hypoglycemia, delayed blood coagulation, ataxia sedation, and labored breathing (Haley, 1965). Even symptoms of acute poisoning with REEs vanish rapidly after excretion from the blood stream (Nakamura et al., 1991a,b).

The REE concentrations in teeth mirror the REE supply of an individuum by liquids (Brown et al., 2004; Evans, 1990; Fernandez-Gavarron et al., 1988; Molleson, 1988). The REEs are supposed to reduce the risk of caries by hardening the enamel and antimicrobial effect (Arai et al., 1991; Zhang et al., 1999).

Milk and eggs show the highest La content, while the highest Ce content is found in meat, fish, and shellfish (Table 10.6). Mean concentrations of La decrease from 4.34 mg/kg in milk and eggs, 2.99 mg/kg in meat, fish and shellfish, 0.184 mg/kg in vegetables and fruits to 0.597 mg/kg in cereals and cereal products (Table 10.3). In comparison Ce concentrations decrease from 3.57 mg/kg in meat, fish, and shellfish, 3.08 mg/kg in vegetables and fruits, 0.593 mg/kg in milk and eggs to 0.436 mg/kg in cereals and cereal products (Table 10.3).

Modeling data show that a standard diet yields the lowest daily input of the REEs Ce and La (Table 10.6). It is remarkable is that low mineralized bottled waters provide relatively the highest input to the diet (Table 10.6).

From different water sources low mineralized bottled waters are prime suppliers of La (Table 10.6). The highest Ce concentrations can be found in tap water. In highly mineralized water the Ce concentration is 2.5 times higher than in low mineralized water (Table 10.6). Independent of the water source, vegans have the highest Ce and La intake, particularly if they consume low mineralized bottled water (Table 10.6). The recommended limit value for REEs in drinking water is 2 μg/L in the Netherlands (De Boer and Lammertsma, 2012).

Changes of dietary habits with respect to liquids have only minor effects on the daily intake of Ce and La as the contribution to the total dietary intake is extremely small (Table 10.6) with <0.01%.

Table 10.6 Mean Ce, La, and Cu Exposure Estimates for Different Water Consumer Types in Different Dietary Group Scenarios

Scenario	**Abbreviation**	**Ce (μg/day)**	**La (μg/day)**	**Cu (μg/day)**
Consumed water type				
Tap water	1 TW	0.150	0.012	158
German bottled mineral water	2 GBW	0.024	0.044	6.9
World bottled mineral water	3 WBW	0.056	0.058	12.5
Low mineralized bottled water	4 LMBW	0.132	0.156	0.36
Highly mineralized bottled water	5 HMBW	0.054	0.028	0.06
Dietary style				
Standard	I	1633	1665	2670
Vegetarian, ovo-lacto	II	2771	2520	2146
Vegan	III	4255	2658	3258
Carnivore	IV	2715	2375	5994
Daily intake				
Minimum daily intake (water type + dietary style)		2 + I	1 + I	5 + II
Minimum daily intake (μg/d)	A	1633	1665	2146
Minimum daily intake scenario: contribution of water (%) to daily intake		<0.002	<0.008	<0.003
Maximum daily intake scenario: water type + dietary style		1 + III	4 + III	1 + IV
Maximum daily intake (μg/day)	B	4255	2658	6152
Maximum daily intake scenario: contribution of water (%) to daily intake		<0.004	<0.006	<0.001

Personal Intake Strategy	**Formula**			
Maximum reduction potential (%) of daily intake	(A/B*100) − 100	−61	−37	−65
Maximum increase potential (%) of daily intake	(B/A*100) − 100	+161	+60	+187

10.3.5 Copper (Cu)

Copper (Cu) is an essential trace element for all living organisms maintaining the functions of various proteins and metallo-enzymes. Cu becomes toxic at higher concentrations (US EPA, 1987; ATSDR, 1990, 2004). High levels of Cu can occur in drinking water as a result of the corrosion of plumbing materials (US EPA, 1987) causing gastrointestinal, hepatic, and renal effects (ATSDR, 2004; US AF, 1990). Accumulation of Cu in tissues can cause a genetic disorder and *Wilson* disease, both considered as chronic Cu toxicity effects (Goyer, 1991; US EPA, 1987). Besides Zn, Cu is the only element which occurs in tap water in higher concentrations than in mineral waters (Table 10.6).

A meat-rich diet delivers 2.8 times more Cu than an ovo-lacto vegetarian diet. A consumer of highly mineralized bottled waters will have the lowest Cu intake of 0.06 μg/day while this value is as high as 158 μg/day if the water is replaced by German tap water (Table 10.6). The contribution of drinking water to the daily Cu intake of a tap water drinking standard diet consumer is 5.6%. The maximum reduction potential for the daily Cu intake through a change of water drinking and dieting habits is correspondingly −65%.

10.3.6 Fluorine (F)

When speaking about F in a nutritional context it is consistently the fluoride anion which is referred to. In relation to the dose F can be beneficial, therapeutic, or toxic. F is mainly incorporated in bones and teeth (Quattrini et al., 2016). F is considered to play a major role in caries prevention. For this reason F is supplemented in many countries like the United States by adding F to the drinking water (Mittelsdorf, 2010; Walsh et al., 2010). In Germany concerns about negative health effects of F by an oversupply is prevailing so the permissible F content in bottled mineral waters and tap water is limited to 5 mg/L F (MTVO, 2006; BfR, 2006).

F is a key medical factor in caries prevention (Rieben and Kielbassa, 2006), but an oversupply may cause dental fluorosis in children (Maciejewska et al., 2006; Murphy, 2008; Yan et al., 2007). Symptoms of F toxicity in children (doses >5 mg/kg F) include nausea, vomiting, and diarrhea (Trube, 2004).

Vegetables and fruits show the highest mean F concentration with 4.44 mg/kg F followed by meat, fish, and shellfish with 2.26 mg/kg F, milk and eggs with 1.70 mg/kg F, and cereals & cereal products with 1.06 mg/kg (Table 10.3). Highly mineralized bottled waters supply >650 μg/L of F which is six times more than that supplied by tap water (Table 10.4).

To comply with the recommended daily intake of 3.5 mg/day F (DGE, 2013) a 30-year-old adult would have to consume more than three times the medically recommended amount of highly mineralized waters. A standard diet supplies about two-thirds of the recommended daily F intake (Table 10.7). Vegan dieters have the highest daily F intake; in combination with highly mineralized waters it doubles the daily recommended F intake (Table 10.7). The choice of the consumed water type is an efficient contribution to increase the daily F intake.

Table 10.7 Mean F, Li, and Mo Exposure Estimates for Different Water Consumer Types in Different Dietary Group Scenarios

Scenario	**Abbreviation**	**F (μg/day)**	**Li (μg/day)**	**Mo (μg/day)**
Consumed water type				
Tap water	1 TW	222	40.6	0.646
German bottled mineral water	2 GBW	782	1820	1.38
World bottled mineral water	3 WBW	1018	656	2.58
Low mineralized bottled water	4 LMBW	896	10.02	34.8
Highly mineralized bottled water	5 HMBW	1348	21.0	2120
Dietary style				
Standard	I	2236	115	340
Vegetarian, ovo-lacto	II	4251	139	493
Vegan	III	6282	205	753
Carnivore	IV	2788	106	401
Daily intake				
Minimum daily intake (water type + dietary style)		1 + I	5 + IV	1 + I
Minimum daily intake (μg/day)	A	2458	127	341
Minimum daily intake scenario: contribution of water (%) to daily intake		9.0	16.5	0.2
Maximum daily intake scenario: water type + dietary style		5 + III	2 + III	5 + III
Maximum daily intake (μg/day)	B	7630	2025	2873
Maximum daily intake scenario: contribution of water (%) to daily intake		17.7	89.9	73.8

Personal Intake Strategy	**Formula**			
Maximum reduction potential (%) of daily intake	(A/B*100) – 100	−68	−94	−88
Maximum increase potential (%) of daily intake	(B/A*100) – 100	+210	+1494	+743

10.3.7 Lithium (Li)

Lithium (Li) is a trace alkali metal. Li is not known to be essential for humans, but was shown to have beneficial health effects. Although considered as a low toxicant to humans the recommendation of EPA for an upper Li concentration in drinking water is <700 μg/L (Aral and Vecchio-Sadus, 2008; Usuda et al., 2007).

The main target of Li toxicity is the nervous system and such detrimental effect occurs preferably during prolonged therapies with Li against bipolar disorders (Kocsis et al., 1993). The symptoms include tremor in hands, lips, and jaws, paralysis, incoherence, stupor, coma, seizure, respiratory and cardiac complication, coma, and death (Gosselin et al., 1984; Hall et al., 1979; OEHHA, 2003). The standard dose of Li carbonate for a chronic therapy of bipolar disorders is 14–28 mg/kg·day (Marcus, 1980).

Differences in the Li concentration between food categories are only small compared to other dietary elements, for instance, B and Ca (Table 10.3). Highest Li concentrations occur in cereals and cereal products with 0.21 mg/kg Li, lowest in meat, fish and shellfish, and milk and eggs with 0.07 mg/kg Li (Table 10.3). A carnivore diet supplies the smallest amount of Li with solid food to the human body (106 μg/day). In a vegan diet the Li intake is almost twice as high. The Li content of water has a strong influence on the Li intake: a consumer of low mineralized bottled water has the lowest (10.02 μg/day) and a consumer of German bottled mineral water has the highest Li intake of 1820 μg/day (Table 10.7). Interesting to note is that German bottled water has higher Li concentrations than the recommended upper limit value of 700 μg/L.

The contribution of drinking water to the daily Li intake is 32.3% for German tap water combined with standard diet and as high as 89.9% in a vegan diet with German bottled water. The maximum reduction/increase potential for the daily Li intake through a change of water drinking and dieting habits is −94% and 1494%, respectively.

10.3.8 Molybdenum (Mo)

Molybdenum (Mo) is an essential trace element for humans and mammals, because it is required for the function of the enzymes xanthine oxidase, aldehyde oxidase, and sulfide oxidase (Rowles, 2017; Rajagopalan, 1988). Mo is a toxic element at high doses, too (Rajagopalan, 1988). An insufficient Cu supply poses a higher risk for Mo toxicity (ACGHI, 1991).

The minimum dietary Mo requirement and the provisional recommended dietary intake of Mo for adults is 0.3 mg/day (WHO, 1993). Mo deficiency in humans is very rare. Reports from China suggest that esophageal cancer is related to Mo deficiency (Blot et al., 1993). Mo toxicity includes symptoms such as fatigue, listlessness, decreased appetite, weakness, headache, anorexia, arthralgia, chest pain, cough, diarrhea, and myalgia (Lesser and Weiss, 1995).

A vegan diet delivers the highest amounts of Mo with 753 μg/day and that of a standard dietary style the lowest with 340 μg/day (Table 10.7). German tap water delivers only 0.646 μg/day Mo, while highly mineralized bottled water provides 2120 μg/day. The contribution of drinking water to the daily Mo intake is 0.19% for a tap water consuming standard dieter and 73.8% for a highly mineralized bottled water consuming vegan. The maximum reduction potential for the daily Mo intake through a change of water drinking and dieting habits is −88% (Table 10.7).

10.3.9 Nickel (Ni)

Nickel (Ni) is considered to be an essential trace element for humans (Anke et al., 1984; Anonymous, 2018; Hausinger, 2018). However, the frequent use of Ni and Ni compounds in everyday life commodities (ATSDR, 2005a; Goyer, 1991; IPCS, 1991) makes Ni intolerance an issue (ATSDR, 2005a). Ni intoxications are caused primarily by inhalation of Ni compounds (ATSDR, 2005a, 2005b; IARC, 1990), especially Ni carbonyl (IPCS, 1991).

The biggest sources of Ni exposure for humans are by ingestion and inhalation from cigarette smoking (WHO, 2000). In addition, humans are exposed to trace amounts of Ni by skin contact with coins and jewelry (HPA, 2009; IARC, 1990). Dermal exposure to Ni or water-soluble Ni salts may cause dermatitis (IPCS, 1991).

A standard and carnivore dietary styles supplies smallest amount of Ni with solid food to the human body (266 and 271 μg/day) whereas a vegan diet delivers 624 μg/day. A consumer of low mineralized bottled mineral water has the lowest Ni ingestion (1.40 μg/day) while world bottled water provides nearly six times more Ni (Table 10.8).

The contribution of drinking water to the daily Ni intake is 0.5% for low mineralized bottled water consuming standard dieter and 1.3% for a world bottled mineral water consuming vegan. The maximum reduction potential for the daily Ni intake through a change of water drinking and dieting habits is −58% (Table 10.8).

10.3.10 Phosphorus (P)

Phosphorus (P) in the form of hydroxalapatite ($Ca_5[OH/(PO_4)_3]$) is an essential component of the hard tissues of bones and teeth in mammals (Lautenschläger et al., 2007). The human body contains about 600–700 g P of which 85% is allocated to such hard tissues (Emsley, 2011; Stegemann and Davis, 2007). Phosphates are constituents of nucleic acids and drivers of the energy metabolism (Bertau et al., 2013; Woehrl, 2008).

P deficiency causes drowsiness, nausea, and cardiac insufficiency (Ackermann, 2011; Brunelli and Goldfarb, 2007). Under long-term conditions of P deficiency humans suffer from arthritis and osteoporosis (Jahnen-Dechent, 2004).

Oversupply with P causes loss in sensibility, cramps, calcification of soft tissues, hypertension, and arrhythmia (Ackermann, 2011).

Table 10.8 Mean Ni, P, and Pb Exposure Estimates for Different Water Consumer Types in Different Dietary Group Scenarios

Scenario	Abbreviation	Ni (µg/day)	P (µg/day)	Pb (µg/day)
Consumed water type				
Tap water	1 TW	7.48	167	2.14
German bottled mineral water	2 GBW	7.38	124	1.38
World bottled mineral water	3 WBW	8.20	102	1.82
Low mineralized bottled water	4 LMBW	1.40	156	7.80
Highly mineralized bottled water	5 HMBW	6.48	123	14.3
Dietary style				
Standard	I	266	3.82×10^6	87.1
Vegetarian, ovo-lacto	II	394	5.30×10^6	145
Vegan	III	624	6.01×10^6	224
Carnivore	IV	271	4.89×10^6	113
Daily intake				
Minimum daily intake (water type + dietary style)		4 + I	3 + I	2 + I
Minimum daily intake (µg/day)	A	267.4	3.82×10^6	88.5
Minimum daily intake scenario: contribution of water (%) to daily intake		0.52	<0.0001	1.6
Maximum daily intake scenario: water type + dietary style		3 + III	1 + III	5 + III
Maximum daily intake (µg/day)	B	632.2	6.01×10^6	238
Maximum daily intake scenario: contribution of water (%) to daily intake		1.3	<0.0001	6.0
Personal Intake Strategy	**Formula**			
Maximum reduction potential (%) of daily intake	(A/B*100) – 100	−58	−36	−63
Maximum increase potential (%) of daily intake	(B/A*100) – 100	+136	+57	+169

Acute P intoxication in humans is unknown. P oversupply in children is related to the attention-deficit hyperactivity disorder (ADHD) syndrome (Hafer, 1998), cardiovascular disease (Rindlisbacher, 2012; Yamamoto et al., 2013; Bozic et al., 2014), and amyotrophia (Wada et al., 2015). The recommended upper daily P intake varies between 700 and 1250 mg (Berdanier, 2002; Mayo Clinic, 2015).

In general, the P concentration of plant products is only half of animal products (Table 10.3). Highest P concentrations are found in milk and eggs with 7944 mg/kg P, lowest in cereals and cereal products with 3153 mg/kg P (Table 10.3).

Tap water has distinctly higher P concentrations than mineral waters, which is supposedly due to the fact that water suppliers add phosphates for corrosion protection (Table 10.8, EPA, 2008). Of all the elements presented in this section P shows the largest difference in supplies by solid food and water sources (Table 10.8). The contribution of liquids to the daily P intake is neglectable with <0.01% (Table 10.8). Only a change of the basic dieting habits may help to reduce P oversupply by one-third (Table 10.8).

10.3.11 Lead (Pb)

Lead (Pb) is one of the most common heavy elements interfering with environmental quality and human health. Despite its manifold uses in chemistry and techniques Pb has exclusively negative effects on living organisms. Aside from occupational or accidental cases lead toxicity is mainly of chronic nature from ingestion of contaminated food and liquids. Chronic Pb poisoning has been phased or ruled out by banning leaded fuels, lead paints and dyes, and lead pipes in drinking water supplies (ATSDR, 2007b).

Exposure to Pb or Pb compounds over a long period of time can cause headache, nausea, vomiting, lethargy, anemia, irritably, high blood pressure, kidney, or liver damage (HPA, 2016; WHO, 2000). The US EPA reported a positive relationship between blood pressure and blood Pb levels in middle-aged men (RAIS, 1997) and acute nephropathy (WHO, 2000). Chronic Pb exposure may cause adverse effects on the reproductive functions of males, for instance, reduced libido and sperm mobility, low sperm counts, and low semen volume (ATSDR, 1999; IPCS, 1995; WHO, 2000). Neurological effects of Pb intoxication are sleep disturbance, headache, fatigue, irritability, convulsions, lethargy, slurred speech, muscle tremors, weakness, and paralysis (IPCS, 1995; ATSDR, 1999). Epidemiological studies assumed that there are no completely safe levels of Pb exposure. Children who are exposed to Pb as a fetus and as toddlers may have encephalopathic symptoms, lower IQ, nerve damage, delayed growth, and behavioral problems (NIH, 2014). Other chronic Pb effects are anemia and decreased hemoglobin synthesis (IPCS, 1995; ATSDR, 1999).

A carnivore and standard diet supply the smallest amounts of Pb with solid food to the human body (87.1 and 113 μg/day) whereas a vegan diet delivers up to 2.6 times more Pb (Table 10.8). Pb concentrations were lowest in German and world bottled mineral waters (Table 10.8). The Pb concentration in low and highly mineralized bottled water was 3.6 and 6.7 times higher than in German tap water. A consumer of German bottled mineral waters will have the lowest Pb intake with 1.38 µg/day (Table 10.8).

The contribution of drinking water to the daily Pb intake is 1.6% for a German bottled water consuming standard dieter and 6.0% for highly mineralized bottled water drinking vegan (Table 10.8). The maximum reduction potential for the daily Pb intake through a change of water drinking and dieting habits is −63% (Table 10.8).

10.3.12 Strontium (Sr)

Strontium (Sr) is a nonessential element with an uncharted toxicity, at least for its stable isotopes. ^{90}Sr unfolds a significant radiotoxicity, but does not occur naturally (Emsley, 2011; Jung, 2007).

Sr is omnipresent in the environment and was shown to have some beneficial effects on human health. Overall, 90% of the Sr inventory of the human body is allocated to bones and teeth, because of its chemical similarity with Ca (Bertau et al., 2013). Sr in the dental element seems to be a reason for a lesser susceptibility against cavity (Losee et al., 1974; Schroeder, 1992). An additional Sr supply is administered to persons suffering from osteoporosis or is given prophylactically to females in the postmenopause to increase bone density (Emsley, 2011).

In odontology hypersensible necks of teeth are treated with Sr salts such as $SrCl_2$ and $Sr(C_2H_3O_2)_2$ (Selent, 2010). Enhanced Sr concentrations in water supplies are suspected to be the reason for a lower prevalence for caries in some regions of the United States (Buddecke, 1981). Special tooth pastes, for example, Sensodyne Rapid advertise the $Sr(C_2H_3O_2)_2$ content as an aid against dental hypersensibility (Mason et al., 2010).

A vegan diet delivers about three times more Sr than a carnivore or standard diet (Table 10.9). The reason for this is that the dietary group vegetables and fruits contain more than twice as much Sr as animal and cereal products (Table 10.3).

Sr is a prominent element in highly mineralized bottled waters while the Sr concentration of low mineralized and tap water are in the same dimension (Table 10.9). Thus vegetarians and vegans with a drinking habit for highly mineralized bottled waters have a two to three times higher daily Sr intake than standard diet consumers (Table 10.9). The highest contribution of water to the daily Sr supply is 22.3% if highly mineralized bottled water is consumed with a standard diet (Table 10.9).

Despite predominantly positive effects of an oversupply, Sr may show negative effects on the bone development in juvenile and adolescent individuals (Emsley, 2011). In this case a change of dietary habits to less vegetables and fruits and a preference of tap or low mineralized bottled waters assists to correct the Sr balance (Table 10.9).

Table 10.9 Mean Sr, U, and Zn Exposure Estimates for Different Water Consumer Types in Different Dietary Group Scenarios

Scenario	Abbreviation	Sr (μg/day)	U (μg/day)	Zn (μg/day)
Consumed water type				
Tap water	1 TW	602	3.34	302
German bottled mineral water	2 GBW	4808	6.16	1.46
World bottled mineral water	3 WBW	1982	7.08	28.8
Low mineralized bottled water	4 LMBW	258	1.90	2.90
Highly mineralized bottled water	5 HMBW	10,788	1.72	15.08
Dietary style				
Standard	I	37,532	1.314	11,103
Vegetarian, ovo-lacto	II	79,359	1.433	9923
Vegan	III	116,447	2.019	12,875
Carnivore	IV	40,606	1.633	16,661
Daily intake				
Minimum daily intake (water type + dietary style)		4 + I	5 + I	4 + II
Minimum daily intake (μg/day)	A	38,134	3.034	9926
Minimum daily intake scenario: contribution of water (%) to daily intake		0.7	56.7	0.3
Maximum daily intake scenario: water type + dietary style		2 + III	3 + III	1 + IV
Maximum daily intake (μg/day)	B	121,255	9.099	16,963
Maximum daily intake scenario: contribution of water (%) to daily intake		4.0	77.8	1.8

Personal Intake Strategy	Formula			
Maximum reduction potential (%) of daily intake	(A/B*100) − 100	−69	−67	−42
Maximum increase potential (%) of daily intake	(B/A*100) − 100	+218	+200	+71

10.3.13 Uranium (U)

Uranium (U) is a naturally occurring radioactive heavy metal especially found in waters derived from sandstone bedrocks (Knolle et al., 2011). U is applied in considerably large quantities through mineral phosphate fertilizers to agricultural land (Kratz et al., 2011) and showed the highest vulnerability to leaching into groundwater

(Smidt et al., 2011). U damages organisms through its chemical toxicity and radioactivity, with the chemical toxicity seen as the primary health hazard. U damages the DNA not only through its own α-emission but also through β-particles emitted as a result of the photoelectric effect which occurs from the interference of the heavy metal U with ambient γ-radiation (Busby and Schnug, 2008).

The main health concerns with respect to U focus on kidneys, reproductive organs, bone growth, DNA, and brain damage. In humans U is particularly known for its nephrotoxic nature, with short-term and long-term exposure to U through drinking water leading to renal effects (Brugge and Buchner, 2011). The information available on the chronic health effects caused by the exposure to U in drinking water points to the fact that in regions with elevated groundwater U concentrations and a higher groundwater use the incidence of certain diseases like, for instance, CKD is increasing (Chandrajith et al., 2010; Wagner et al., 2011). U is an endocrine-disrupting chemical leading to an increased risk of fertility problems (Raymond-Wish et al., 2007).

Kidneys are the main target for chemical U toxicity of peak concentrations during the excretion process. Radiation is of particular risk for lungs and bones. The liver and spleen are prominent places of U accumulation. The most remarkable effect of U toxicity going along with low and medium U contamination is cancer. Meanwhile increasing rates of kidney failure in humans over the last 20 years have been associated, at least partially, to the drastic increase in mineral water consumption, which causes a considerably higher U intake (Schnug et al., 2005). Schnug and Lindemann (2006) found that between 1986 and 2004 with a certainty of 97% both the mineral water consumption and the frequency of kidney replacement therapy in Austria, Germany, and the United States have increased by the same extent (approximately 5% per year).

U shows the smallest range of daily elemental intake among the four dietary groups (Table 10.9). A standard diet supplies the smallest amount of U with solid food to the human body (1.314 μg/day) whereas a vegan diet delivers the highest amount with 2.019 μg/day. A consumer of low and highly mineralized bottled water has the lowest (1.72 and 1.90 μg/day) and a consumer of German and world bottled mineral waters has the highest U intake with 6.16 and 7.08 μg/day, respectively (Table 10.9). In Germany, a limit value of 2 μg/L exists for bottled mineral water which is suitable for the preparation of baby food and an action value of 20 μg/L in drinking water (MTVO, 2006; Trinkw, 2006). A general limit value of 10 μg/L has been notified for drinking water (Anonymous, 2011a).

The contribution of drinking water to the daily U intake of a tap water drinking standard diet consumer is 71.8% with a range of 56.7% for a highly mineralized bottled water to 84.3% for a world bottled mineralized water consumer. The maximum reduction potential for the daily U intake through a change of water drinking and dieting habits is −67%.

10.3.14 Zinc (Zn)

Zinc (Zn) is an essential element for human nutrition. It is essential for the function of >300 enzymes, predominantly dehydrases and proteases (Stefanidou et al., 2006).

Zn deficiency in humans has general symptoms such as hypogonadism, night blindness, mental lethargy, retarded growth, anorexia, loss of appetite, decreased sense of taste and smell, slow wound healing, and skin changes (Prasad, 1983). It can also impair the immune system (Baer et al., 1985). A common symptom of acute oral exposure to Zn compounds is gastrointestinal distress, abdominal cramps, nausea, vomiting, diarrhea, headache, and lethargy (ATSDR, 2005b). Gastrointestinal bleeding and hematological signs of anemia also go along with high doses of Zn (RAIS, 1992).

Zn shows a distinct variation of the daily intake in relation to the dietary styles (Table 10.9). An ovo-lacto vegetarian diet supplies the smallest amount of Zn with solid food to the human body (9923 μg/day) whereas a carnivore diet delivers 16,661 μg/day. Compared to the Zn intake by solids that by water is only small (Table 10.9). A consumer of German bottled mineral water will have the lowest (1.46 μg/day) and a consumer of German tap water will have the highest Zn intake with 302 μg/day (Table 10.9). The contribution of drinking water to the daily Zn intake for a tap water drinking standard diet consumer is 2.6%. The maximum reduction potential for the daily Zn intake through a change of dieting and drinking habits is −42%. As mentioned previously the dietary style offers the biggest opportunity to influence the Zn intake.

10.4 Conclusions

In Table 10.10 recommended/required and tolerable elemental intake data are listed and set in relation to the elemental intake by a standard diet and the contribution of different mineral waters and tap water to the daily intake (data listed in Tables 10.5–10.9).

The results of the study show that the TDI values for As and Ca are exceeded by the daily intake with solid food (Table 10.10). In the case of Li and Mo German bottled mineral water and highly mineralized bottled water provide 1820 μg/day Li and 2120 μg/day Mo (Table 10.7) so the TDI values are exceeded by these water types. A change of the consumed water type is an easy way to reduce the intake of these elements. Solid food provides more Ni than recommended so a change of dietary habits is the most efficient way to adjust the intake. With the

Table 10.10 Daily Intake of As, B, Ca, Ce, Cu, F, La, Li, Mo, Ni, P, Pb, Sr, U, and Zn by Humans With a Standard Diet and Percentage of Different Sources of Water of the Daily Intake in Relation to Benchmark Values

	Rec./req.[a] Intake	TDI[b]	Standard Diet	Percentage of Water of Daily Intake (%) Consumed Water Type[c]				
Element	**(µg/day)**	**(µg/day)**	**(µg/day)**	**TW**	**GBW**	**WBW**	**LMBW**	**HMBW**
As		146	447	0.57	0.85	7.7	1.3	**9.5**
B	1350	20,000	2847	2.8	13.8	32.1	3.7	**54.7**
Ca^{2}	1000	2500	2532	5.0	10.5	5.8	1.0	**22.2**
Ce		3000	1633	**0.009**	0.002	0.003	0.008	0.003
Cu	900	10,000	2670	**5.6**	0.26	0.47	1.3	0.002
F	3500	10,000	2236	9.0	25.9	31.3	28.6	**37.6**
La		3000	1664	0.0007	0.003	0.003	0.009	0.002
Li	1000	1800	115	32.3	**94.1**	85.1	8.0	15.4
Mo	325	630	340	0.19	0.40	0.75	9.3	**86.2**
Ni	250	1000	266	2.7	2.7	**3.0**	0.52	2.4
P	7×10^{5}	3×10^{6}	3.82×10^{6}	**0.004**	0.003	0.003	0.004	0.003
Pb		309	87.1	2.4	1.6	2.0	8.2	**14.1**
Sr		1,500,000	37,532	1.6	11.4	5.0	0.68	**22.3**
U			1.314	71.8	82.4	**84.3**	59.1	56.7
Zn	11,000	45,500	11,103	**2.6**	0.013	0.26	0.026	0.14

Bold values indicate the water type which provides the highest daily contribution to the mineral intake.

TW, tap water; GBW, German bottled water; WBWC, world bottled water; LMBW, low mineralized bottled water; HMBW, highly mineralized bottled water.

[a] Rec./req., recommended/required intake.

[b] TDI, tolerable daily intake for a 70 kg person (EPA, 2008; Kaye, 2018; Weeden et al., 2014).

[c] mg/day.

consumption of German and world bottled mineral water the consumer ingests >80% of the daily U intake. Striking is that in the case of U water will contribute to at least 56.7% of the daily U intake of a person together with a standard diet. In some regions of Germany drinking water contains naturally high U concentrations (Smidt et al., 2011). Neither decantation nor filter equipment for household use is able to remove U from the drinking water. For large-scale application ion exchange systems are available, but they are expensive and produce follow-up problems. Filters show an increased radioactivity not only from U, but also from its much more hazardous decay product radon over time (Jekel et al., 2007). Despite this it makes not much sense to clean-up tap water of which at the maximum 3% is used for dietary purposes. Overall, 97% of the tap water consumed by a private household ends up in bathroom sinks, toilets, dish washers, and washing machines. A much more efficient strategy is to advise consumers to replace the water needed for direct drinking and preparation for drinks and foods with bottled waters with a certified low U content. The German consumer has online access to individual data about the U concentration in tap water in different regions, and mineral water through Strahlentelex (Anonymous, 2011b). Considering the significant amounts of U applied annually with mineral P fertilizers to agricultural land the risk of an entry of U into the food chain has been named and loads were calculated (Smidt et al., 2011). Recent research showed that not only shallow groundwaters in the upper aquifers are at risk of contaminations by fertilizer-derived U, but also deeper water bodies which have been rated as being geologically protected and safe, and finally suitable for the production of bottled mineral waters (Knolle et al., 2011; Popit et al., 2004).

Legislative bodies all over the world are generally very reluctant when it comes to reducing the environmental loads of heavy metals. Although it is meanwhile known since long that P-fertilization in agriculture is the only relevant source for U loads to water bodies (Kratz et al., 2011), neither Germany (Cordts, 2011; Leiterer, 2011) nor any other country in the world limits the U content in P fertilizers. This is particularly astonishing as the removal of U during the manufacturing process of P fertilizers is an old and well-proven technology (Schnug and Haneklaus, 2011). A legit limitation of the U content in P fertilizers in the fertilizer ordinance has been suggested (Ekardt and Schnug, 2011) as it would be the most promising measure to protect drinking water worldwide from further, continuous U contamination and to conserve this cheap and healthy beverage for future generations.

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11

SIGNIFICANCE OF GEOGRAPHICAL, HYDROGEOLOGICAL, AND HYDROGEOCHEMICAL ORIGIN FOR THE ELEMENTAL COMPOSITION OF BOTTLED GERMAN MINERAL WATERS

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11.1 Introduction

Classifications provide a priori information about an object's features and each classification system has its own purpose. Wellwaters and groundwaters were subjected to numerous classification systems (Gerb, 1958; Hölting and Coldewey, 2011; Mattheß and Ubell, 1983; Mattheß, 1994; Van der Aa, 2003; Sirocko, 2012). The historic types go nearly 200 years back to Hufeland (1820) and describe primarily the effects of waters on human health and well-being (Carlé, 1975; Käß and Käß, 2008).

[☆] *In memoriam Inge Lindemann (May 3, 1958–August 4, 2011)*: Inge Lindemann was a passionate and ambitious investigative journalist and humanist who dedicated much of her work to uranium in mineral waters. Without her constant admonitions, Germany would be a long way from regulations for uranium in drinking waters.

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The German mineral and table water ordinance (Min/TafelWV, 2017) categorizes by origin and functional specifications. Stratigraphic (geological) and hydrogeological categories describe regional origins, in contrast to hydrogeochemical categories which address chemical group features.

All classification systems have in common that one or more distinctive attributes are used for the classification. However, little is known about the added information about the parameters which are not used for classifying. In case of mineral waters, this is primarily their elemental composition which can be appraised just from the attribution to a specific group of a distinct classification system.

The regional hydrogeology of Germany is elaborately described (Ad-hoc-Arbeitsgruppe Hydrogeologie, 2016), but rarely in context with the chemical composition of its waters. Groundwaters and especially mineral waters are the vehicle transporting the elements from the geological bedrock into the human food chain and thus are also an important factor soil components have on human health via agricultural production (Nieder et al., 2018). The significance to retrieve the additional knowledge behind water classifications has practical reasons, for example, to assess the vulnerability of deep groundwater to environmental pollution and the sanitary evaluation of waters in medical geology (Selinus, 2013).

11.2 Elemental Concentrations in Bottled German Mineral Waters

Table 11.1 shows the descriptive statistics of elemental concentrations in the latest version of the mineral water data base maintained at the Institute for Crop and Soil Science (JKI-PB), Julius Kühn-Institut in Braunschweig (Fig. 11.1). Basically mineral waters show always higher elemental concentrations than tap waters, with the exception of Cu and Zn (Holzhausen, 2016). Bottled mineral waters are characterized by relatively high concentrations (mg/L) of Na (159), Cl (152), Ca (149), S (89.1), Mg (44.5), K (12.5), and Si (8.0). Elevated levels are typical of the trace elements (μg/L) Sr (2404), F (391), and Ba (330), too. In contrast, rare earth elements occur in low concentrations with maximum values of up to 0.050 μg/L for Lu 0.030 for Eu and Ho and 0.020 for In, Tb, and Tm. In total, the lowest concentrations of 50 out of 67 elements are below the limit of quantification of the analytical methods employed. Because of the large variability of the corresponding primary and secondary minerals in the rock material, the different elements in mineral waters show a broad range in the variability of their concentrations (Table 11.1).

Table 11.1 Descriptive Statistics of Chemical Elements in 637 German Mineral Waters

Element	Unit	Minimum	Maximum	Mean	Median	Variance	95. Percentile	Standard Deviation	Variation Coefficient (%)
Ag	µg/L	<NG	0.070	0.005	0.001	0.001	0.030	0.01	213
Al	mg/L	<NG	281	7.26	4.00	266	22.0	16.3	224
As	µg/L	<NG	51.1	1.20	0.280	14.0	5.31	3.74	311
B	µg/L	2.20	2610	194	70.4	113,401	747	337	173
Ba	µg/L	0.45	140,000	330	32.7	37,000,000	233	6085	1842
Be	µg/L	<NG	10.1	0.110	0.005	0.510	0.230	0.71	673
Bi	µg/L	<NG	0.350	0.003	0.003	0.001	0.005	0.02	451
Br	µg/L	1.50	3149	135	45.5	101,963	520	319	235
Ca	mg/L	1.40	794	149	94.4	21,585	519	147	99
Cd	µg/L	<NG	0.440	0.020	0.004	0.002	0.070	0.04	282
Ce	µg/L	<NG	0.560	0.020	0.010	0.002	0.080	0.05	210
Cl	mg/L	0.800	16,590	152	33.2	602,935	487	776	510
Co	µg/L	<NG	6.47	0.120	0.020	0.240	0.320	0.49	416
Cr	µg/L	<NG	5.96	0.49	0.100	0.590	2.07	0.77	156
Cs	µg/L	<NG	119	3.16	0.090	105	17.0	10.2	324
Cu	µg/L	<NG	117	1.51	0.280	63.2	4.42	7.95	528
Dy	µg/L	<NG	0.130	0.004	0.002	0.001	0.010	0.01	259
Er	µg/L	<NG	0.100	0.004	0.001	0.001	0.010	0.01	262
Eu	µg/L	<NG	0.030	0.002	0.001	0.001	0.010	0.0	155
F	µg/L	0.400	3480	391	248	184,446	1190	429	110
Fe	µg/L	<NG	9945	103	3.45	398,638	365	631	615
Ga	µg/L	<NG	0.040	0.004	0.003	0.001	0.010	0.0	105
Gd	µg/L	<NG	0.130	0.004	0.002	0.001	0.010	0.01	254
Ge	µg/L	0.010	11.1	0.180	0.040	0.460	0.640	0.68	369
HCO_3^-	mg/L	<NG	55,946	592	344	5,100,000	1515	2259	382
Hf	µg/L	<NG	0.260	0.058	0.001	0.001	0.020	0.02	381

Continued

Table 11.1 Descriptive Statistics of Chemical Elements in 637 German Mineral Waters—cont'd

Element	Unit	Minimum	Maximum	Mean	Median	Variance	95. Percentile	Standard Deviation	Variation Coefficient (%)
Hg	µg/L	<NG	0.200	0.040	0.030	0.001	0.100	0.03	89
Ho	µg/L	<NG	0.030	0.001	0.001	0.001	0.010	0.0	187
I	µg/L	0.360	766	11.9	5.38	1844	31.3	42.9	362
In	µg/L	<NG	0.020	0.00	0.002	0.001	0.010	0.0	126
K	mg/L	0.100	1401	12.5	3.70	3567	34.0	59.7	477
La	µg/L	<NG	0.230	0.010	0.010	0.001	0.010	0.02	174
Li	µg/L	<NG	13,300	162	35.3	457,863	692	677	417
Lu	µg/L	<NG	0.050	0.001	0.001	0.001	0.00	0.0	299
Na	mg/L	0.460	12,870	159	25.2	378,792	552	615	387
Mg	mg/L	0.530	4196	44.5	26.0	29,673	106	172	387
Mn	µg/L	<NG	1559	42.8	1.94	21,931	210	148	346
Mo	µg/L	<NG	11.1	0.760	0.300	1.97	2.78	1.40	184
Nb	µg/L	<NG	0.810	0.020	0.005	0.003	0.070	0.06	297
Nd	µg/L	<NG	0.320	0.010	0.005	0.001	0.040	0.02	216
Ni	µg/L	0.010	25.9	1.98	0.460	13.3	9.78	3.65	184
P	µg/L	1.98	759	61.8	53.0	3270	138	57.2	93
Pb	µg/L	<NG	1.81	0.140	0.100	0.05	0.420	0.21	147
Pr	µg/L	<NG	0.060	0.002	0.001	0.001	0.010	0.0	183
Rb	µg/L	0.100	410	14.1	3.88	1171	56.5	34.2	242
S	mg/L	<NG	7139	89.8	19.0	103,771	417	322	359
Sb	µg/L	<NG	2.28	0.160	0.060	0.060	0.540	0.23	150
Sc	µg/L	0.010	8.85	0.330	0.090	0.750	1.42	0.87	260
Se	µg/L	<NG	4.94	0.200	0.040	0.220	0.97	0.47	231
Si	mg/L	1.25	40.3	7.99	6.70	25.9	16.2	5.09	64
Sm	µg/L	<NG	0.100	0.001	0.001	0.001	0.010	0.01	228
Sn	µg/L	<NG	1.80	0.020	0.010	0.010	0.040	0.10	444

Sr	µg/L	8.00	220,000	2404	526	997,000,000	9383	9987	415
Ta	µg/L	<NG	0.110	0.004	0.002	0.001	0.010	0.01	163
Tb	µg/L	<NG	0.020	0.001	0.001	0.001	0.001	0.001	172
Te	µg/L	<NG	1.34	0.040	0.020	0.010	0.110	0.100	274
Th	µg/L	<NG	0.190	0.005	0.002	0.001	0.020	0.010	268
Ti	µg/L	<NG	9.20	0.350	0.130	0.560	1.24	0.750	213
Tl	µg/L	<NG	0.950	0.020	< NG	0.010	0.090	0.090	357
Tm	µg/L	<NG	0.020	0.0009	0.0005	–	0.0025	0.00183	–
U	µg/L	<NG	27.4	1.27	0.240	7.81	6.53	2.79	220
V	µg/L	0.01	5.22	0.290	0.140	0.290	1.07	0.540	182
W	µg/L	<NG	4.07	0.120	0.030	0.230	0.400	0.480	390
Y	µg/L	<NG	1.37	0.050	0.020	0.010	0.180	0.100	224
Yb	µg/L	<NG	0.220	0.005	< NG	0.00	0.020	0.020	329
Zn	µg/L	<NG	293	5.77	2.40	269	17.4	16.4	284
Zr	µg/L	<NG	48.7	0.720	0.040	18.7	1.64	4.33	605

Remarks:
JKI-PB water database last updated 12.12.2017.
<NG: below the practical lower limit of quantification ($X_{BG} = y_B + 9s_B$; y_B = mean of blank value; s_B = standard deviation of blank value).
X_{BG} in µg/L (decreasing order): HCO_3^-, Na, K: 4000–250; Si, P, Ca, Mg, P, S, Cl, F, Br, Sr: 100–1; Rb, Al, B, Ba, Li, Zn, Mn: 0.6–0.2; Fe, Ti, Cu, Ge, V, Mo, Cr, Zr, Te, Ni: 0.150–0.020; Se, W, U, Be, Ga, Hg, Cs, Pb, Sn, Bi, Cd, Co, Y, Ta, Ag, As, Dy, Eu, Gd, La, Nb, Nd, Dy, Hf, Tl, Yb, Sc, Sm, Th, Er, Ho, Lu, Pr, Tb, Tm, Ce, Sb: 0.005–0.002 µg/L.
To avoid statistical distorting "0" value concentrations measured below X_{BG} in this table were set to $0.5 \times X_{BG}$ (Birke et al., 2010).

Fig. 11.1 The mineral water collection (part of) at the Institute for Crop and Science of Julius Kühn-Institut. Photo: Silvia Haneklaus, Julius Kühn-Institut.

With regard to the variation coefficients Ba, Fe, and Zr show the largest variability; in contrast, much lower ones have Ca, P, Hg, and Si (Table 11.1). Fig. 11.2 displays the ranking of the elements in mineral waters according to the variability of their concentration.

11.3 Standardization of Elemental Concentrations in Bottled Mineral Waters

For a bias-free comparison of concentrations of different elements in mineral water assigned to different classification procedures, analytical data have to be standardized. A widely adopted procedure is reported by Hötzl (1982):

$$n_{ij}^{x} = \frac{\left(x_{ij} - x_{i,\min}\right)}{\left(x_{i,\max} - x_{i,\min}\right)}$$

with

x_{ij} = concentration element "*i*" in the sample "*j*"

$x_{i,\min}$ = minimum elemental concentration in the entire database

$x_{i,\max}$ = maximum elemental concentration in the entire database

n_{ij}^{x} = standardized variable for an element in the database

Fig. 11.2 Elements in 637 German mineral waters, ranked according to the increasing coefficients of variation.

According to this transformation, a value of 0.000 corresponds with the lowest standardized value, because the enumerator is 0.000. In practice, a value of 0.000 is set when the normalized variable is <0.00045. Accordingly, the standardized maximum of 1.000 is set if the variable exceeds ≥0.995. Both values assign the lowest and highest elemental concentration after standardization. By all means, the standardized value “0.000” can correspond to a measured value larger than the lower limit of quantification. Simply its stray occurrence in the entire dataset makes the value set to 0.000. According to this, the values “0” and “1.000” may occur repeatedly in different groups of a classification system.

Standardized data have no dimensions. In order to differentiate in the following text real measurement data from standardized ones, the first are designated with “element concentrations” and the second ones as “relative elemental concentrations.” In the following text, only results are represented where differences between classes of a classification system proved to be significant in the F-test. However, the reader shall keep in mind that significance in the F-test does not necessarily mean that also the mean values between the classes are statistically significantly different. It only indicates that the classification is a significant source of variance.

11.4 Significance of the Geological Origin of Bottled Mineral Waters

The probably most easy classification of bottled mineral waters is by their hydrogeological origin in relation to the geological and stratigraphic situation at the source (Ad-hoc-Arbeitsgruppe Hydrogeologie, 2016). The youngest stratigraphic formation from which mineral water is sourced in Germany is from the Quaternary, beginning 2.6 million years ago. The oldest one is from the Proterozoic more than 2500 million years ago (Table 11.2). When classified by geological age of the source rock 22 elements showed significant (F-test) differences in their concentrations in German mineral waters. More than half of the elements with elevated concentrations can be found in sources with bedrocks from the Paleozoic and Proterozoic (Table 11.3), namely Be, Cs, Er, F, Ge, Lu, Mo, Sb, Si, Tm, U, Yb, and HCO_3^- (Fig. 11.3).

In waters from younger strata, that is, the Quaternary and Tertiary, neither strikingly high, nor low concentrations occur. One reason is

Table 11.2 Stratigraphic Allocation for Classification and Statistical Analysis According to Knolle (2008, extended)

Beginning (Million Years Before Present)	Period	Class, Used in the Statistical Analysis		
2.6	Quaternary	Quaternary		
66	Tertiary	Tertiary		
145	Cretaceous	Cretaceous		
201	Jurassic	Jurassic		
252	Triassic	Triassic		
299	Permian	Permian		
359	Carboniferous	Carboniferous	Devonian-Carboniferous	
419	Devonian	Devonian		
444	Silurian	Silurian	Proterozoic-Cambrian-Ordovician-Silurian	
485	Ordovician	Ordovician		Proterozoic-Cambrian-Ordovician
541	Cambrian	Cambrian		
>2500	Proterozoic	Proterozoic		

Table 11.3 Standardized Elemental Concentrations (Dimensionless) in German Mineral Waters Sampled in Different Stratigraphic Units

Stratigraphic Unit	Element																					
	B	Be	Ca	Cs	Er	F	Ge	Hg	La	Lu	Mo	Nb	Ni	Rb	S	Sb	Si	Tl	Tm	U	V	Yb
Devonian	0.83	0.03	0.38	0.60	0.18	0.10	0.95	1.00	0.64	0.14	0.05	0.75	1.00	0.87	0.09	0.34	0.28	0.85	0.10	0.05	0.33	0.16
Devonian-Carboniferous	0.00	0.01	0.00	0.00	0.09	0.30	0.00	[a]	0.97	0.00	0.31	0.01	0.06	0.00	0.00	0.00	0.76	0.00	0.00	0.05	0.69	0.06
Jurassic	0.81	0.00	0.84	0.17	0.08	0.30	0.19	0.24	0.54	0.02	0.60	0.33	0.28	0.43	0.58	0.53	0.02	0.18	0.03	0.13	0.23	0.05
Cambrian	0.01	0.34	0.06	0.14	0.07	0.21	0.06	[a]	0.01	0.02	0.00	0.01	0.29	0.07	0.03	0.13	0.72	0.00	0.00	0.00	0.04	0.06
Carboniferous	0.21	0.02	0.42	0.08	0.07	0.22	0.43	0.00	0.08	0.01	0.92	0.03	0.34	0.17	0.05	0.36	0.40	0.13	0.04	0.17	0.01	0.05
Cretaceous	0.65	0.00	0.37	0.01	0.02	0.04	0.14	0.29	0.00	0.01	0.22	0.00	0.08	0.05	0.11	0.31	0.09	0.01	0.20	0.13	0.02	0.00
Ordovician	0.04	0.26	0.19	0.37	0.01	0.44	0.38	0.15	0.07	0.00	0.13	0.02	0.00	1.00	0.03	0.07	0.59	0.03	0.00	0.06	1.00	0.01
Permian	1.00	0.02	0.75	0.44	0.38	0.41	0.25	0.49	1.00	0.33	0.73	1.00	0.12	0.73	0.17	0.32	0.00	0.46	0.37	0.22	0.33	0.37
Proterozoic-Cambrian-Ordovician	0.50	0.50	0.64	0.87	0.23	1.00	1.00	0.60	0.18	0.17	1.00	0.15	0.46	0.90	0.31	1.00	0.41	0.81	0.16	1.00	0.07	0.22
Proterozoic-Cambrian-Ordovician-Silurian	0.54	0.06	0.59	1.00	1.00	0.37	0.32	0.60	0.18	1.00	0.05	0.13	0.32	0.71	0.01	0.18	0.39	0.20	1.00	0.03	0.00	1.00
Proterozoic	0.02	1.00	0.03	0.25	0.09	0.00	0.15	[a]	0.73	0.00	0.04	0.01	0.32	0.36	0.06	0.05	1.00	0.02	0.00	0.02	0.09	0.02
Quaternary	0.29	0.01	0.36	0.02	0.05	0.05	0.09	0.37	0.13	0.04	0.23	0.06	0.16	0.08	0.16	0.27	0.16	0.07	0.06	0.08	0.10	0.5
Tertiary	0.13	0.00	0.34	0.25	0.00	0.01	0.10	0.60	0.41	0.00	0.36	0.60	0.04	0.40	0.02	0.23	0.17	0.60	0.01	0.15	0.65	0.01
Triassic	0.53	0.08	1.00	0.14	0.15	0.27	0.13	0.46	0.23	0.06	0.63	0.09	0.42	0.27	1.00	0.33	0.02	1.00	0.09	0.55	0.24	0.09

[a] Not enough data.

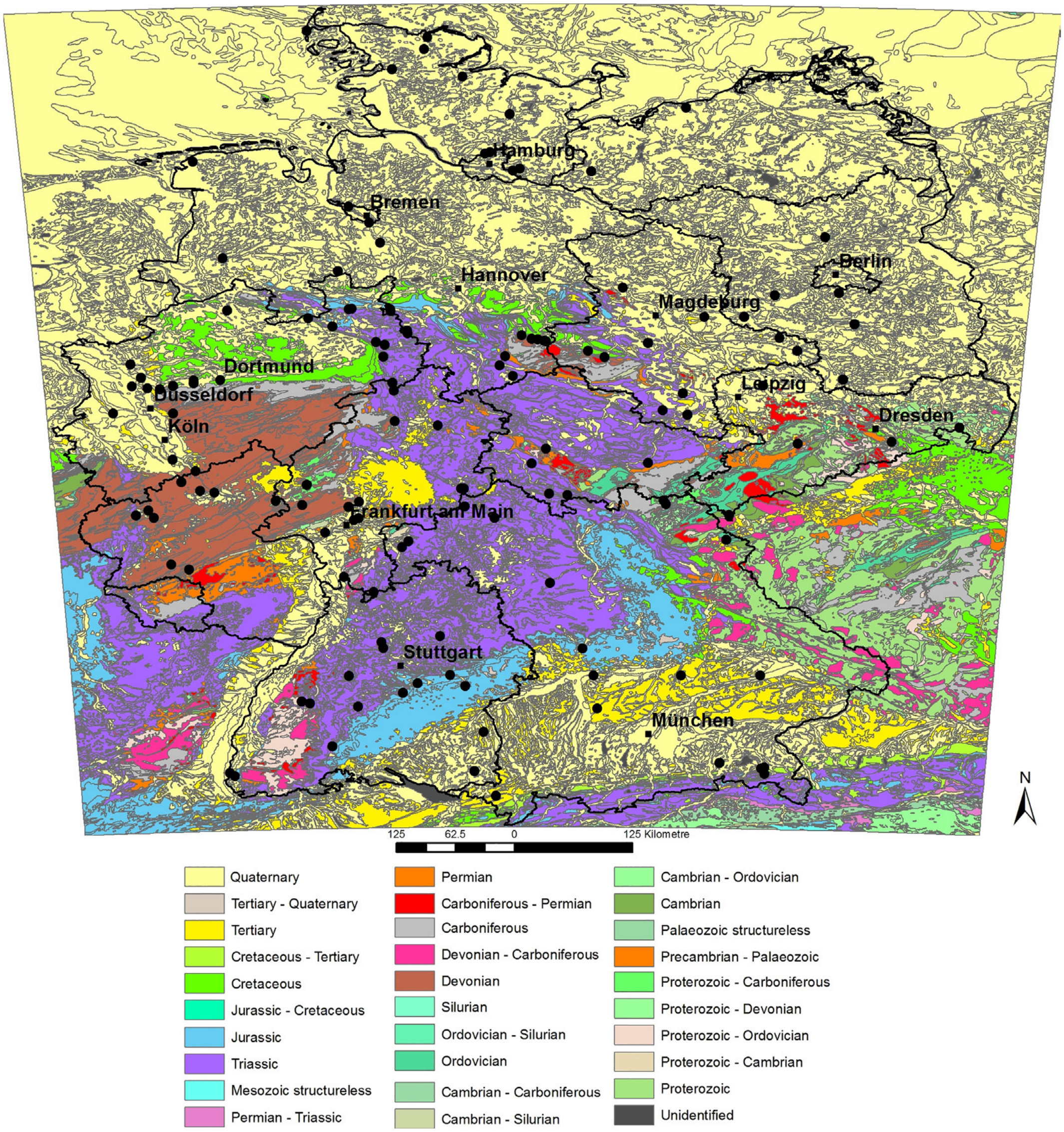

Fig. 11.3 Geological map of Germany with geocoded locations of mineral water sources. Note: The alleged distortion is the result of using WGS84 coordinates for positioning, the map is true to scale. For attribution of the sources, the leading stratigraphic rock formation was chosen. Data extracted from Knolle, F., 2008. Ein Beitrag zum Vorkommen und Herkunft von Uran in deutschen Mineral- und Leitungswässern. PhD Thesis, Braunschweig. https://publikationsserver.tu-braunschweig.de/receive/dbbs_mods_00027200 (Accessed 24 January 2018); Richts, A., Vierhuff, H., 2002. Hydrogeologische Regionen. In: BMU (Ed.), Hydrologischer Atlas von Deutschland (HAD), 2. Lfg., Table 5.1, Bonn.

most likely the increasing weathering and time of contact between bedrock and water. Another one, but true only for radioactive elements is the substantial loss of mass through radioactive decay over geologic periods. During the 2.5 Ga between the Proterozoic and Quaternary, the mass loss of the primordial radioisotope U due to radioactive decay is detectable. The half-life of the most abundant U isotope ^{238}U (99.3%) is for instance 4.47 Ga (Roesler and Lange, 1975). Consequently, waters from sources on older bedrock (Paleozoic/Proterozoic) have a higher U concentration than the ones from younger rock (Quaternary and Tertiary) (Table 11.3).

11.5 Significance of the Hydrogeological Origin of Bottled Mineral Waters

Hydrogeology is the area of geology that investigates the distribution and movement of groundwater in the soil and rocks of the Earth's crust (commonly in aquifers). In hydrogeology, the aquifer-bearing rocks are divided and classified in regions and subregions which for Germany are displayed in Fig. 11.4.

From 67 elements quantified in German mineral waters, the variability of 20 concentrations revealed to be significantly (F-test) different between the hydrogeological classes. Only five mineral water sources in the database are located in the hydrogeological region 1 "Coast." In this category, the mineral waters show the relatively lowest concentration of Cs, Hg, Se, and U (Table 11.4).

Compared to mineral waters sourced in the hydrogeological region 2 ($n = 185$), those from the region 3 ($n = 306$) show elevated concentrations of As, B, Ca, Cs, Er, F, Ge, Hf, Hg, K, La, Li, Lu, Mo, Nb, Ni, Rb, S, Se, Si, U, Y, Yb, and Zr (Table 11.4). Only I is elevated in mineral waters from the region 2 (Table 11.4).

Mineral waters from the region 3 ($n = 306$) and those sourced from region 2 have relatively high concentrations of As, Ca, K, Mo, S, Se, U, and Y, whereas those from region 4 are characterized by elevated concentrations of B, Cs, Er, F, Ge, Hf, Hg, La, Li, Lu, Nb, Ni, Rb, Si, Yb, and Zr (Table 11.4).

Hydrogeological regions in Germany are subdivided by stratigraphic features (Tables 11.5–11.7). Also, between stratigraphic subclasses, the variability of elemental concentrations in German mineral waters is significantly different (Tables 11.5–11.7).

The hydrogeological region 2 is a large landscape mostly situated in Germany's northern lowlands formed by the Pleistocene. The locations are further classified (Table 11.5). Typical for their hydrogeology are yieldingly porous aquifers which range throughout main parts of northern Germany. Water flows in the porous space of unconsolidated

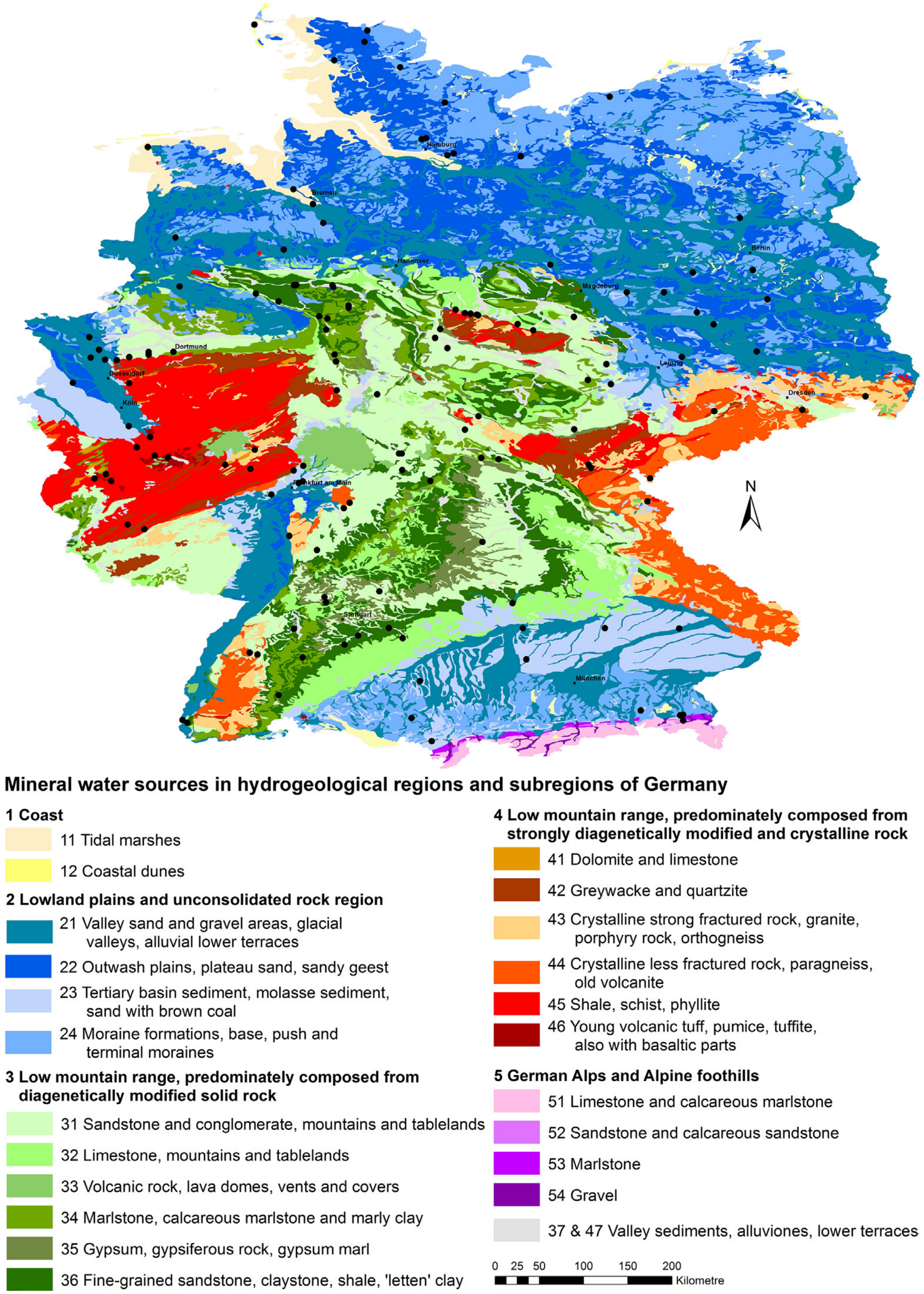

Fig. 11.4 Hydrogeologic regions and subregions in Germany, and geocoded locations of sampled mineral waters. Data extracted from Knolle, F., 2008. Ein Beitrag zum Vorkommen und Herkunft von Uran in deutschen Mineral- und Leitungswässern. PhD Thesis, Braunschweig. https://publikationsserver.tu-braunschweig.de/receive/dbbs_mods_00027200 (Accessed 24 January 2018); Richts, A., Vierhuff, H., 2002. Hydrogeologische Regionen. In: BMU (Ed.), Hydrologischer Atlas von Deutschland (HAD), 2. Lfg., Table 5.1, Bonn.

Table 11.4 Standardized Elemental Contents (Dimensionless) in Mineral Waters Classified by Hydrogeological Regions in Germany

Hydrogeological Region/Element	As	B	Ca	Cr	Cs	Er	F	Ge	Hf	Hg	Ho	I	In	K	La	Li	Lu	Mo	Nb	Ni	Rb	S	Se	Si	Th	U	Y	Yb	Zr
German Alps and Alpine foothills (*n*=5)	0.622	0.000	0.000	0.066	0.000	0.000	0.000	0.000	0.000	n.d.	0.000	0.382	n.d.	0.000	0.000	0.000	0.000	0.485	0.000	0.000	0.000	0.000	0.039	0.000	0.000	0.430	0.000	0.000	0.000
Lowland plains and unconsolidated rock region (*n*=185)	0.000	0.391	0.054	0.000	0.171	0.120	0.517	0.183	0.003	0.130	0.101	1.000	0.000	0.345	0.638	0.179	0.085	0.048	0.484	0.016	0.253	0.098	0.109	0.524	0.156	0.180	0.342	0.126	0.025
Coast (*n*=5)	0.008	0.471	0.432	1.000	0.000	0.979	0.311	0.015	0.114	0.000	1.000	0.689	1.000	0.520	0.630	0.015	0.463	0.255	0.013	0.072	0.076	0.495	0.000	0.661	1.000	0.000	0.789	0.597	0.042
Low mountain range, predominately composed from diagenetically modified solid rock (*n*=306)	1.000	0.965	1.000	0.185	0.199	0.613	0.977	0.232	0.322	0.128	0.663	0.000	0.041	1.000	0.550	0.572	0.482	1.000	0.211	0.356	0.354	1.000	1.000	0.395	0.536	1.000	1.000	0.517	0.297
Low mountain range, predominately composed from strongly diagenetically modified and crystalline rock (*n*=136)	0.413	1.000	0.162	0.165	1.000	1.000	1.000	1.000	1.000	1.000	0.616	0.703	0.043	0.881	1.000	1.000	1.000	0.000	1.000	1.000	1.000	0.156	0.351	1.000	0.407	0.496	0.993	1.000	1.000

n.d., no data.

Table 11.5 Overview of the Range of Standardized Elements (Dimensionless) in Mineral Water Samples of the Hydrogeological Region 2 According to Richts and Vierhuff (2002)

Hydrogeological Region	Stratigraphic Examples	Regional Examples	Contents[a]
Lowland plains and unconsolidated rock region	Valley sand and gravel areas, glacial valleys, alluvial lower terraces	Pre-Weichsel: Northern Germany Weichsel: Northern Germany Lower Rhine Bay Upper Rhine Graben Alpine foothills	Min.: Zr, La Max.: no elements
	Outwash plains, plateau sand, sandy geest	Pre-Weichsel: Northern Germany Weichsel Northern Germany Rhein-Main-Neckar area	Min.: S, U, Li, Na, Mg, B, Cl, Cr, Cs, F, and HCO_3 Max.: no elements
	Tertiary basin sediment, molasse sediment, sand with brown coal	Rhineland Northern and Central Germany Rhein-Main area Bavaria	Min.: Si Max.: La, Nb
	Moraine formations, base, push and terminal moraines	Pre-Weichsel: Northern Germany Weichsel: Northern Germany Alpine foothills	Min.: Er, Ge, Hf, Ho, Mn, Rb, Si, and Y Max.: no elements

[a] Elements with relatively lowest (min.) and highest (max.) levels.

rock, and the water flow follows hydraulic gradients, partly through up to 500 m deep Pleistocene channels (Ortlam and Vierhuff, 1978). To this region belongs also the Tertiary basin deposits of the northern Upper Rhine area, the Cologne Bay, the Wetterau area at the foothills of the Rhenish Slate Mts., as well as parts of the Alpine foreland (Richts and Vierhuff, 2002).

The hydrogeological region 3 consists predominately of slightly diagenetically modified bedrock originating from the Mesozoic era. To this region belong limestone, marl, gypsum, and clastic rock. Waters from regions with gypsum and anhydrite show increased sulfate

Table 11.6 Overview of the Range of Standardized Elements (Dimensionless) in Mineral Water Samples of the Hydrogeological Region 3 According to Richts and Vierhuff (2002)

Hydrogeological Region	Stratigraphic Examples	Regional Examples	Contents[a]
Low mountain range, predominately composed from diagenetically modified solid rock	Sandstone and conglomerate, mountains and tablelands	Mostly waters from Bunter sandstone, Rotliegend waters from Saarland and Nordpfalz	Min.: no elements Max.: no elements
	Limestone, mountains, and tablelands	Hard and very hard water	Min.: As, La, Mo, V, and W Max.: Hf, Mg
	Volcanic rock, lava domes, vents, and covers	Usually rock with very low TDS, range of hardness from very soft to relatively hard waters	Min.: As, La, Mo, V, and W Max.: Hf, Mg
	Marlstone, calcareous marlstone, and marly clay	Rock with high TDS, e.g., Permotriassic sediment	Min.: Si Max.: As, B, Ca, Cl, Dy, Fe, Li, and Yb
	Gypsum, gypsiferous rock, and gypsum marl	Salinar rock wide spread in Permian and Triassic, in Lower Saxony also in Upper Jurassic and partly Tertiary	Min.: Hg, Tm Max.: HCO_3, Mg, S
	Fine-grained sandstone, claystone, shale, "letten" clay	Northern German uplands, Thuringian Basin and South Germany with Swabian-Franconian region	Min.: no elements Max.: no elements
	Valley sediments, alluviones, lower terraces	Relatively hard to hard waters with high TDS	Min.: Nb, Ni Max.: no elements

[a] Elements with relatively lowest (min.) and highest (max.) levels.

concentrations (Table 11.6). Sources on sandstone and conglomerates show no element with exceptionally high or low concentration (Table 11.3). Mineral waters sourced from wells in limestone and valley sediment show minimal concentrations for seven elements (As, La, Mo, V, W, Nb, and Ni). In waters from wells in valley sediment, fine-grained sandstone and mudstone for no element exceptionally high concentrations can be expected.

Table 11.7 Overview of the Range of Standardized Elements (Dimensionless) in Mineral Water Samples of the Hydrogeological Region 4 According to Richts and Vierhuff (2002)

Hydrogeological Region	Stratigraphic Examples	Regional Examples	Contents[a]
Low mountain range, predominately composed from strongly diagenetically modified and crystalline rock	Greywacke and quartzite	Rhenish Slate Mts., Harz Mts., Thuringia	Min.: Fe Max.: In, P
	Crystalline strong fractured rock, granite, porphyry rock, and orthogneiss	Odenwald, Harz Mts., high parts of plutonite und metamorphite, granular disintegration zones along jointed rock	Min.: no elements Max.: Ho, Lu, Er, Tm, and Yb
	Crystalline less fractured rock, paragneiss, and old volcanite	Deeper parts of plutonite and metamorphite	Min.: no elements Max.: Be, Cs, F, Mo, Si, and U
	Shale, schist, and phyllite	Erzgebirge, Harz Mts., Rhenish Slate Mts.	Min.: no elements Max.: Ge, Ni, and Rb
	Young volcanic tuff, pumice, tuffite, also with basaltic parts	Eifel, Swabian Alb, Vogelsberg, Hegau, and Laacher See tuff	Min.: As, Lu, Mo, V, and W Max.: Mg, Hf

[a] Elements with relatively lowest (min.) and highest (max.) levels.

In contrast, when sourced from volcanic rock waters are likely to have maximum concentrations of Mg and Hf (Table 11.4). Waters from marlstone regions are characterized by maximum concentrations of Mg, As, B, Ca, Cl, Dy, Fe, Li, and Yb.

Predominately strongly diagenetically modified crystalline bedrock formed by intense transformation processes characterizes the region 4. The structure of this rock is compact and water moves predominately through fissures. Hydraulic permeability depends at large on fissure size, the degree of separation, compactness, and deformation. Weathered rock material may form porous space for water. With increasing depth, the opening width of fractures decreases in these regions and consequently also the groundwater capacity.

Mineral waters from the region 4 contain only elements with maximum concentrations, however, none with minimum ones (Table 11.7).

11.6 Significance of the Hydrogeochemical Classification of Bottled Mineral Waters

The hydrogeochemical classification describes the chemistry of groundwaters, particularly the relationship between the chemical characteristics and quality of waters and the regional geology. A common classification of waters based on hydrogeochemical differences is the method according to Piper (1944), based on the work of Hill (1942) and Langelier and Ludwig (1942) (see Zaporozec, 1972). A so-called Piper plot (Fig. 11.5) is a trilinear diagram, which was primarily developed to visualize the relative abundance of common ions

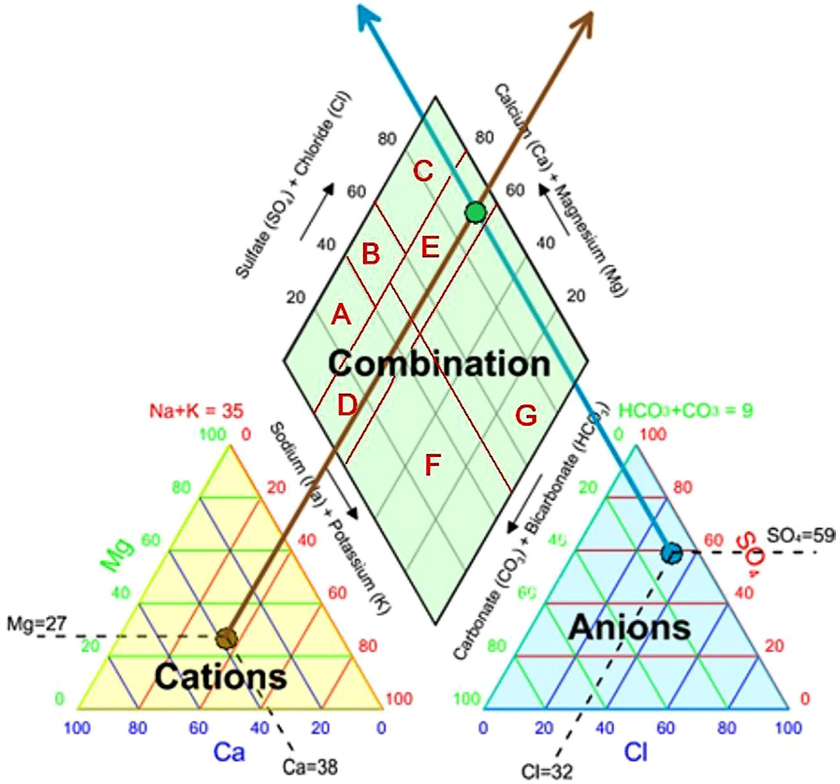

Fig. 11.5 The three components and interpretation of Piper plots. Notes: Bottom left is a ternary plot of the cations, bottom right is a ternary plot of the anions, and top is a diamond plot of a projection from the other two plots (Golden, 2017); *red lines* in the diamond plot designate the seven Piper classes (see Table 11.8); main Piper groups: "normal alkaline earth waters" = A–C; "alkaline earth waters with higher alkali content" = D–E; "alkaline waters" = F–G. Modified from Golden, 2017. What Is a Piper Plot (Trilinear Diagram)? https://support.goldensoftware.com/hc/en-us/articles/115003101648-What-is-a-piper-plot-trilinear-diagram- (Accessed 5 February 2018).

in water samples (Srinivasa Rao, 1998; Dissanayake and Chandrajith, 2009). Although there are other plot types that can show the abundance of ions in groundwater, this plot type is especially useful because it allows to plot multiple samples in the same plot, thus allowing for grouping water samples by groundwater facies and other criteria (Golden, 2017).

A Piper plot (Fig. 11.5) comprises three components: a ternary diagram in the lower left representing cations (magnesium, calcium, and sodium plus potassium), a ternary diagram in the lower right representing anions (chloride, sulfate, and carbonate plus bicarbonate), and a diamond plot in the middle which is a matrix transformation of the two ternary diagrams. Each sample is normalized to 100 (sum of cations = 100, sum of anions = 100), so the relative concentrations are on a percentage basis.

The diamond plot in Fig. 11.5 can be used to classify waters. Samples attributed to the fields "A–C" are classified as "normal alkaline earth waters," the ones matching the areas "D–E" are classified as "alkaline earth waters with higher alkali content" and the ones in "F–G" belong to the main Piper group "alkaline waters."

Samples in the top quadrant are calcium sulfate waters, which are typical of gypsum groundwater and mine drainage. Samples in the left quadrant are calcium bicarbonate waters, which are typical of shallow fresh groundwater. Samples in the right quadrant are sodium chloride waters, which are typical of marine and deep ancient groundwater. Samples in the bottom quadrant are sodium bicarbonate waters, which are typical of deep groundwater influenced by ion exchange (Golden, 2017).

The Piper classification addresses the chemical composition of waters while it reveals no information about a geographical, geological, or hydrogeological background. German mineral waters classify to 9% into "mainly hydrogen carbonatic," 15% into "hydrogen carbonatic-sulfatic," 3% into "mainly sulfatic," 35% into "mainly hydrogen carbonatic," 3% into "mainly sulfatic," 31% into "mainly (hydrogen) carbonatic," and 13% into "mainly sulfatic-chloridic" waters of the Piper classification (Table 11.8).

Most of the German mineral waters are classified as "mainly hydrogen carbonatic" (Piper group "D"). Statistical analysis of the relative elemental concentrations in German mineral waters reveals that the concentration of 44 elements is statistically different (F-test) between hydrogeochemical classes (Table 11.9). This number is twice as high as the number of elements identified as significant between stratigraphic classes (Section 11.4).

In alkaline waters 32 elements show relatively high concentrations (Table 11.10), among them are rare earth elements. Reason for this might be the complexation of lanthanides with inorganic and

Table 11.8 Classification of Water in Main Groups and Classes According to Piper

Piper Main Group	Piper Class	Description
Normal alkaline earth waters	A	Mainly hydrogen carbonatic
	B	Hydrogen carbonatic-sulfatic
	C	Mainly sulfatic
Alkaline earth waters with higher alkali content	D	Mainly hydrogen carbonatic
	E	Mainly sulfatic (chloride <20 mmol (eq)—%)
		Mainly chloridic (chloride >50 mmol (eq)—%)
Alkaline waters	F	Mainly (hydrogen) carbonatic
	G	Mainly sulfatic-chloridic (hydrogen carbonate <50 mmol (eq)—% chloride >50 mmol (eq)—%)
		Mainly chloridic (hydrogen carbonate <20, chloride >70 mmol (eq)—%)

organic ligands which increases their solubility, reactivity, mobility, and chemical fractionation in the environment (Shan et al., 2002; Ding et al., 2005; Tang and Johannesson, 2003). Particularly environmentally relevant are the elements As and Cd and their concentrations are extremely high with 51.1 (As) and 0.440 (Cd) µg/L (Table 11.1). The only elements with extreme low relative concentrations in alkaline waters are Ca and Te (Table 11.10). In contrast, mineral waters classified as "alkaline earth waters with higher alkali content" reveal no increased concentration with any element except Sb (Table 11.10). However, 24 elements, among these As and Cd, show their relatively lowest concentration in waters classified as "alkaline earth waters with higher alkali content." Characteristic for this water type are obviously low concentrations of S and high ones of Ca and Te (Table 11.10).

The picture changes when the three Piper main groups are further differentiated in seven classes (Tables 11.11 and 11.12 and Fig. 11.5). Table 11.12 is an extraction of Table 11.11 designating elements with extreme concentrations in the different Piper classes. Comparing the results presented in Tables 11.10 and 11.12 reveal that the number of elements with distinctly low or high concentrations decreases when the number of classes increases. This says that the additional information on elemental concentrations in mineral waters retrievable from a certain classification system is not only dependent on the kind of classification system, but also on its internal structure.

In total, 41 elements show significantly different concentrations in mineral waters from the different Piper classes (Table 11.12). The tungsten (W)

Table 11.9 Standardized Elemental Contents (Dimensionless) in German Mineral Waters Attributed to the Three Piper Main Groups

Piper Main Group	Al	As	B	Be	Br	Ca	Cd	Cl	Cs	Dy	Er	F	Fe	Ga	Ge	Hf	I	K
Normal alkaline earth waters	0.12	0.72	0.39	0.00	0.00	1.00	0.58	0.00	0.00	0.00	0.00	0.29	0.42	0.00	0.09	0.16	0.25	0.01
Alkaline earth waters with higher alkali content	0.00	0.00	0.00	0.05	0.13	0.07	0.00	0.02	0.01	0.14	0.19	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Alkaline waters	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

La	Li	Lu	NO_3^-N	Na	Mo	Nb	Nd	Pr	Rb	S	Sb	Se	Si	Te	Th	Ti	W	Yb	Zn	Zr
0.14	0.02	0.00	0.22	0.00	1.00	0.04	0.15	0.24	0.00	1.00	0.00	1.00	0.00	1.00	1.00	0.22	0.03	0.00	0.48	0.01
0.00	0.00	0.20	0.00	0.03	0.00	0.00	0.00	0.00	0.01	0.00	1.00	0.00	0.52	0.09	0.00	0.00	0.00	0.16	0.00	0.00
1.00	1.00	1.00	1.00	1.00	0.05	1.00	1.00	1.00	1.00	0.12	0.32	0.67	1.00	0.00	0.49	1.00	1.00	1.00	1.00	1.00

Table 11.10 Overview of the Range of Standardized Elements (Dimensionless) in German Mineral Waters Attributed to the Three Main Piper Groups

	Piper Main Group		
Contents[a]	Normal Alkaline Earth Waters	Alkaline Earth Waters With Higher Alkali Content	Alkaline Waters
Min.	Be, Br, Cl, Cs, Dy, Er, Ga, Lu, Na, Rb, Sb, Si, and Yb	Al, As, B, Cd, F, Fe, Ge, Hf, I, K, La, Li, NO_3^-,N, Mo, Nb, Nd, Pr, S, Se, Th, Ti, W, Zn, and Zr	Ca, Te
Max.	Ca, Mo, S, Se, Te, and Th	–	Al, As, B, Be, Br, Cd, Cl, Cs, Dy, Er, F, Fe, Ga, Ge, Hf, I, K, La, Li, Lu, NO_3^-, N, Na, Nb, Nd, Pr, Rb, Si, Ti, W, Yb, Zn, and Zr

[a] Elements with relatively lowest (min.) and highest (max.) levels.

concentration for instance revealed to be lowest in mineral waters of the type "alkaline earth waters with higher alkali content and mainly hydrogen carbonatic or sulfatic" (Table 11.11). Same is true for Mo in waters of the "mainly hydrocarbonic alkaline" type. Reason is most likely the close dependency of Mo and W solubility on the pH and redox status in aquifers (Smedley et al., 2014). All other elements show their relatively lowest and highest concentration always once in each class. Remarkably is that the lowest, respectively highest relative concentration of Al, B, Cs, Fe, Ge, Li, Nd, Pr, Rb, Ti, and Zn occur in "mainly sulfatic-chloridic alkaline" waters (Table 11.12).

A glance at the data presented in Table 11.12 strikes that in the Piper classes "C" and "D" are no elements with relatively high concentrations. In contrast, in the classes "F" and "G" 32 out of in total 39 elements show maximum concentrations.

11.7 Significance of Principal Component Analysis of Bottled Mineral Waters

A common phrase says "lose sight of the wood for the trees," which again is a well-known fact with exploiting big datasets in science. The mineral water and tap water database at Julius Kühn-Institut (Fig. 11.1) is a typical example for a big number of cases and a big number of parameters: looking only at the 637 German specimens, Holzhausen (2016) found that among 67 chemical elements, 45% of all possible correlative combinations turned out to be statistically significant with $P < 0.05$. Of this, again 6.1% showed a correlation coefficient of $r > 0.5$. This says in fact that the variability of one variable explains already at least 25% of the variability of its pairing partner. Principal component analysis (PCA) is a multivariate statistical procedure which reduces the variability observed in a larger number of parameters (e.g., different elemental concentrations in mineral waters) to a smaller straightforward number of so-called but nameless principal components (PCs). The smaller number of PCs carry then the information on the variability of a much larger set of variables and due to this make an interpretation easier, let relation between and cluster of variables emerge clearer (Husson et al., 2009).

In contrast to PCA, discriminant analysis (DA) identifies combinations of variables which are best suited to differentiate between individual groups of case/parameter combinations (Härdle and Simar, 2007).

Multivariate statistical methods have been employed for the generation of maps demonstrating the quality of surface (An et al., 2016; Ayeni and Soneye, 2013; Udayakumar et al., 2009) and groundwaters (Subyani and Al Ahmadi, 2009), the classification of mineral waters (Lourençoa et al., 2010) and the identification of mineralization process in groundwaters (Petersen et al., 2001; Rehman et al., 2016). In this chapter, multivariate statistical methods are demonstrated to identify elements which have the strongest classification power in stratigraphical, hydrogeological, and hydrogeochemical classification systems. As multivariate statistical methods are still not very common in applied science, the following paragraphs communicate the very basics of PCA and DA.

The objective of PCA is to reduce the information observed in a larger number of variables to a smaller number of so-called "PCs" or "factors" (Gaensslen and Schubö, 1976; Schuchard-Ficher et al., 1982). Imagine the PCs as an orthogonal axis in a Cartesian coordinate systems, says the correlation between the PCs is "0."

In detail, a PCA has the following steps (SPSS, 2017):

- standardization of the initial data matrix so that $\overline{x} = 0$ and $s^2 = 1$;
- calculation of the correlation matrix; and
- extraction of PCs.

Factors are linear combinations of all variables in a data matrix with the general formula:

$$F_A = W_{1A}x_1 + W_{2A}x_2 + \cdots + W_{nA}x_m$$

where W_{nA} is the weight of variable x_m in PCA.

The correlation between a factor and a variable is called the "loading" of a variable on a PC. PCA is an algorithm where the weights for a PC are chosen to maximize its explained variability for the entire set of variables. The sum of the squared loadings on a PC is called its eigenvalue.

Table 11.11 Standardized Elemental Contents (Dimensionless) in German Mineral Waters Samples Attributed to Piper Classes (Description in Table 11.8)

Piper Class	Al	As	B	Be	Br	Ca	Cd	Cl	Cs	Dy	Er	F	Fe	Ga	Ge	Hf	I
A	0.21	1.00	0.43	0.01	0.07	1.00	0.00	0.08	0.01	0.00	0.00	0.28	0.17	0.00	0.07	0.22	0.60
B	0.16	0.00	0.71	0.00	0.08	0.71	1.00	0.03	0.04	0.15	0.05	0.46	0.53	0.32	0.19	0.09	0.12
C	0.14	0.01	0.09	0.05	0.00	0.19	0.24	0.00	0.06	0.15	0.14	0.35	0.12	0.30	0.04	0.09	0.00
D	0.17	0.06	0.05	0.08	0.06	0.02	0.05	0.02	0.08	0.28	0.28	0.24	0.13	0.14	0.06	0.08	0.06
E	0.00	0.01	0.00	0.01	0.18	0.15	0.07	0.07	0.00	0.17	0.16	0.00	0.00	0.29	0.00	0.00	0.06
F	0.62	0.19	0.99	1.00	0.25	0.00	0.41	0.14	0.69	1.00	1.00	0.92	0.12	0.39	0.66	1.00	0.59
G	1.00	0.71	1.00	0.07	1.00	0.07	0.95	1.00	1.00	0.99	0.78	1.00	1.00	1.00	1.00	0.19	1.00

K	La	Li	Lu	Na	Mo	Nb	Nd	Pr	Rb	S	Sb	Se	Si	Te	Th	Ti	W	Yb	Zn	Zr
0.05	0.24	0.03	0.00	0.02	0.62	0.08	0.22	0.39	0.06	1.00	0.00	0.18	0.80	0.30	1.00	0.33	0.02	0.00	0.34	0.01
0.03	0.21	0.05	0.03	0.02	1.00	0.08	0.20	0.30	0.06	0.71	0.27	1.00	0.00	1.00	0.29	0.23	0.01	0.02	0.65	0.01
0.00	0.40	0.00	0.01	0.00	0.22	0.05	0.34	0.32	0.07	0.13	0.41	0.24	0.10	0.23	0.06	0.10	0.03	0.05	0.17	0.05
0.03	0.35	0.03	0.26	0.02	0.02	0.10	0.27	0.29	0.15	0.00	0.48	0.19	0.42	0.09	0.11	0.18	0.00	0.24	0.25	0.04
0.01	0.00	0.00	0.08	0.04	0.00	0.00	0.00	0.00	0.00	0.18	1.00	0.00	0.57	0.06	0.00	0.00	0.00	0.05	0.00	0.00
0.31	1.00	0.46	1.00	0.37	0.00	1.00	0.84	0.88	0.73	0.08	0.11	0.18	1.00	0.06	0.13	0.39	0.39	1.00	0.33	1.00
1.00	0.89	1.00	0.57	1.00	0.08	0.19	1.00	1.00	1.00	0.23	0.67	0.51	0.36	0.00	0.37	1.00	1.00	0.61	1.00	0.06

Table 11.12 Overview of the Range of Standardized Elements (Dimensionless) in German Mineral Waters Attributed to Piper Subgroups (Description in Table 11.8)

	Piper Class						
Contents[a]	A	B	C	D	E	F	G
Min.	Cd, Dy, Er, Ga, Lu, Sb, Yb	As, Be, Si	Br, Cl, I, K, Li, Na	S,W	Al, B, Cs, F, Fe, Ge, Hf, La, Li, Mo, Nb, Nd, Pr, Rb, Se, Th, Ti, W, Zn, Zr	Ca, Mo	Te
Max.	As, Ca, S, Th	Cd, Mo, Se, Te	–	–	Sb	Be, Dy, Er, Hf, La, Lu, Nb, Si, Yb, Zr	Al, B, Br, Cl, Cs, F, Fe, Ga, Ge, I, K, Li, Na, Nd, Pr, Rb, Ti, W, Zn

[a] Elements with relatively lowest (min.) and highest (max.) levels.

The remaining not explained variability results in a first-order residual covariance matrix from which again a second or more PCs can be extracted by the same procedure. The number of PCs extractable from a dataset equals the number of variables in the dataset, but the number of PCs extracted from a dataset is usually limited to those with an eigenvalue >1 (the amount of variable explained by the PCs equals the amount of a variable, a PC with an eigenvalue <1 explains less variability than a single variable and therefore is senseless).

As a rule of thumb in a PCA, the number of PCs with an eigenvalue >1 is approximately 1/3–1/6 of the entire number of variables in a dataset (Gaensslen and Schubö, 1976). In a component loading matrix, all PCs extracted from a dataset summarize the relation between the entire variables and the extracted PCs. Due to their orthogonality, PCs resemble a system of axes within a cluster of analytical data. According to their loadings, the variables arranged in the space spanned by the PCs and empirical units become visible variable clusters. Graphic displays are limited to only three PCs, because the human brain can only visualize three dimensions in space. In so far, PCA proves the existence of hyperspaces (Schnug, 2007). PCA aims to explain as much of the variability of the entire data, by means of minimizing squared distances between variable and PC. Consequently, the extracted PCs are located within the variable clusters. By means of a mathematical procedure called “varimax rotation,” the PCs are shifted from their "squared distance minimizing" position through the variable clusters into a "squared distance maximizing" position between the variable clusters. The varimax rotation has no effect on the mathematical solution of a PCA, but makes the interpretation of the results much easier.

In contrast to PCA which seeks for communalities in clusters of variables, DA aims for identifying linear combinations of variables which separate groups best (Schuchard-Ficher et al., 1982). The main difference between both methods is that in a DA the group membership is a priori established, in PCA not. In a DA, a number of variables are combined in a mathematical function (TUM, 2017). In case of a linear function, the result is called a canonical discriminant function with the discriminating variable y and the characteristic variables X_i:

$$Y = b_0 + b_1x_1 + b_2x_2 + \cdots + b_px_i$$

The coefficients b_1, b_2, ... b_i are called discrimination coefficients while b_0 is a constant. Graphically spoken, a discriminant function is a projection from a p-dimensional feature space in the one-dimensional (1D) space of a discriminant function:

$$y_{jk} = b_0 + b_1x_{1jk} + b_2x_{2jk} + \cdots + b_px_{ijk}$$

Relative standardized discriminant coefficients are the individual standardized discriminant coefficients divided by the sum of the standardized coefficients of a canonical discriminant function. The relative standardized canonical discriminant coefficient describes the relative contribution of a particular discriminant coefficient to the entire discriminating power of a discriminant function.

Table 11.13 presents the result of a PCA of complete 500 consistent data sets with concentrations of 67 elements from the mineral water data base at Julius Kühn-Institut. The PCA extracts in total 19 PCs with an eigenvalue >1 from this dataset, of which each alone explains between 1.54% and 17.5% of the variability observed in the entire data set. All together the 19 PCs explain cumulatively three quarter of the total variability observed in the entire data set (Table 11.13). The first three PCs conjoin already one-third of the total explained variability.

The first PC is primarily loaded by light rare earth elements, a result already observed by Birke et al. (2010). In contrast, the second one by heavier rare earth elements (Table 11.13). The loading on the PCs seems to resemble the similarity in the charge, ionic radius, and electronic shell structure electron structure of the elements (Henderson, 1982; Shannon, 1976).

Elements which are characteristic for clay minerals and feldspars such as Cs and Rb are loading high on the third PC (Table 11.13). Ge is also a high loading element which is not only lithophile, but also sidero- as well as chalcophile and prone to replace Si in silicates (Kabata-Pendias, 2011). PCs are nameless mathematical constructs and their

Table 11.13 Principal Components With an Eigenvalue of >1 and High Loading ($r > 0.8$) Elements Extracted From the Analysis of 500 Data Sets of German Mineral Water Samples Comprising 67 Chemical Elements

Component No.	Eigenvalue	Explained Variance (%)	Cumulative Explained Variance (%)	High Loading Elements ($r > 0.800$)
1	11.5	17.5	17.5	Dy (0.887), Gd (0.959), Nd (0.880), Pr (0.832), Sm (0.948), Y (0.858)
2	5.29	8.02	25.5	Er (0.802), Lu (0.963), Yb (0.950)
3	3.67	5.57	31.2	Cs (0.886), Ge (0.862), Rb (0.892)
4	3.45	5.23	36.3	As (0.844), Fe (0.892)
5	3.33	5.04	41.3	Cl (0.915), Li (0.913), Na (0.892)
6	2.48	3.75	45.1	HCO_3^- (0.981), Mg (0.973), S (0.914)
7	2.25	3.41	48.5	Sc (0.827), Th (0.888)
8	2.00	3.03	51.5	
9	1.89	2.86	54.4	Hf (0.955)
10	1.83	2.77	57.1	Ba (0.983), Sr (0.894)
11	1.71	2.59	59.7	
12	1.57	2.38	62.1	
13	1.46	2.21	64.3	
14	1.40	2.12	66.4	Bi (0.802)
15	1.32	2.00	68.4	
16	1.26	1.90	70.3	Ag (0.810), Te (0.819)
17	1.13	1.70	72.1	
18	1.06	1.61	73.7	
19	1.01	1.54	75.2	

interpretation a process of scientific creativity (Schnug et al., 1993) which obscurity increases with falling contribution of a PC to the total variability explained. Therefore, the interpretation of Table 11.13 ends at this point.

As mentioned before, only three PCs can be graphically displayed at a time. With the large number of variables, the display of the first three PCs of 67 chemical elements in German mineral waters looks promiscuously (Fig. 11.6) but still demonstrates the prominent role of the rare elements in the entire main component solution.

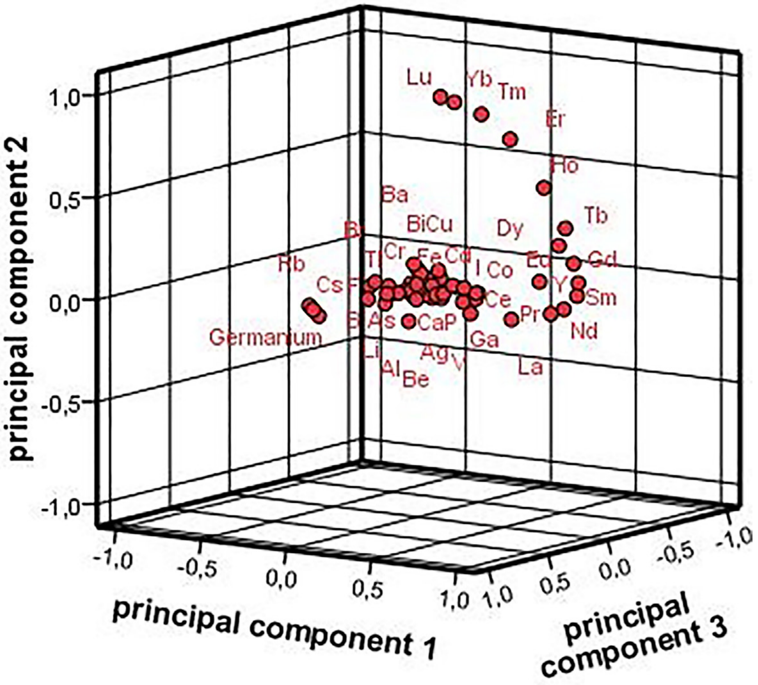

Fig. 11.6 Three-dimensional (3D) illustration of the first three principal components (varimax rotated) in 500 data sets of German mineral water samples with in total 67 elements.

A deeper insight in the role of rare earth element concentrations as a differentiating criteria for classifying mineral waters delivers a DA where the classes attributed to the individual mineral waters are the grouping variable. Table 11.14 displays the relative discriminant coefficients of canonical discriminant functions for differentiating between geological regions (geology based on stratigraphic age), hydrogeological regions and subregions, and Piper main groups and classes.

The figures in Table 11.14 resemble the relative contribution of an element to the differentiating or discrimination power of the function. For the classification by stratigraphy and hydrogeology and for the Piper main groups each one and for the more complex structured Piper classes two significant discriminant functions can be calculated. The best discrimination produces the function for the Piper main groups, where the discriminant function explains 87.2% of the entire variability of the data base, the worst with only 27.3% the discrimination between different stratigraphic classes (Table 11.14). Remarkable is especially the fact that in all seven functions in Table 11.14 only a small number of 10 elements out of 67 are strongest discriminating. 16 elements have multiple occurrence among the first 10 discriminant coefficients in Table 11.14: Lu and Tm (six times), Er, Dy, and Zr (five times), Gd and Sm (four times), Ca, Cs, Hf, Ho, Li, and Rb (three times) as well as Mg, Pr, Y, Yb, and Nd (two times) and at last one time each

Table 11.14 Relative Discriminant Coefficients of Functions for Distinguishing Geological Regions (Geology Based on Stratigraphic Age), Hydrogeological Regions and Subregions, and Piper Main Groups and Classes

Geological Region (Stratigraphic Age)		Hydrogeological Region		Hydrogeological Subregion				Piper Main Group		Piper Class			
				Discriminant Function 1		Discriminant Function 2				Discriminant Function 1		Discriminant Function 2	
Element	**(%)**	**Element**	**(%)**	**Element**	**(%)**	**Element**	**(%)**	**Element**	**(%)**	**Element**	**(%)**	**Element**	**(%)**
Tm	9.36	Tm	9.03	Gd	8.95	Yb	12.6	Dy	7.68	Dy	6.79	Hf	9.24
Dy	8.65	Gd	8.36	Tm	8.75	Tm	8.32	Hf	6.06	Er	5.80	Zr	9.18
Lu	7.70	Er	8.20	Lu	7.77	Lu	6.89	Lu	5.97	Sm	5.53	Ho	8.24
Gd	7.37	Dy	7.73	Dy	6.67	S	4.31	Ho	5.34	Gd	5.07	Tm	7.34
Er	7.25	Lu	5.98	Er	6.55	Ca	3.83	Zr	5.30	Hf	4.90	Lu	6.96
Rb	7.10	Cs	5.67	Rb	4.90	Pr	3.52	K	3.48	Y	4.61	Mg	3.95
Sm	6.29	Rb	5.49	Pr	4.83	Mg	3.44	Li	3.48	Zr	4.45	Pr	3.43
Cs	5.99	Zr	3.63	Cs	4.79	Er	3.34	Na	3.34	Li	4.20	Nd	3.34
Zr	2.75	Sm	3.37	Sm	3.73	Li	2.99	Ca	3.22	Ho	4.19	Ca	3.28
Y	2.68	Y	3.29	Yb	2.88	La	2.88	Nd	2.97	Tm	3.86	Ho	2.99
Explained variability (%)													
	27.3		54.3		22.6		14.8		87.2		49.5		21.8

La, Mg, Na, and S. In contrast, elements with usually higher concentrations in mineral waters like for instance Ca, K, Mg, Na, and S show only in the discriminant functions for the Piper main groups and Piper classes and in the second, less powerful discriminating function, for the hydrogeological subregions (Table 11.14).

Quite obviously especially trace elements determine to a great extent to which class of a particular classification system a particular mineral water belongs.

11.8 Conclusions

Classifications group items according to the common characteristics into categories. For bottled mineral waters, these are in particular characteristics of stratigraphical and hydrogeological origin, and hydrogeochemical typecast. Little is known what additional information about the elemental composition of a mineral water is hidden behind a specific classification. This chapter reveals what additional information about the elemental composition can be found in common classifications of mineral waters.

Knowledge of the stratigraphic category of a source for instance gives evidence of at least 22 elements: if a well is located in geologically older rocks, namely those from wells of the Paleozoic/Proterozoic aquifer age the mineral water is likely to have elevated concentrations of Be, Cs, Er, F, Ge, Lu, Mo, Sb, Si, Tm, U, Yb, and HCO_3^-. In contrast, in waters from younger aquifers of the Tertiary and Quaternary elemental concentrations are usually neither particularly high, nor low (Section 11.4).

In case the hydrogeological classification of a source is known, high concentrations of La and Nb can be expected in waters from wells of regions with unconsolidated sediments which can be typically found in the northern lowlands of Germany. The content of As, Ca, K, S, Se, U, and Y come out highest in water drawn from aquifers of slightly diagenetically modified bedrock found for instance in low mountain ranges. In contrast, the highest contents of B, Cs, Er, F, Ge, Hf, Hg, La, Li, Lu, Nb, Ni, Rb, Si, Yb, or Zr can be expected in waters from wells in strongly diagenetically modified strata and crystalline bedrocks, which are exemplarily for the Harz and Rhenish Slate Mts. (Section 11.5).

A commonly used classification system for waters is the hydrogeochemical Piper classification. But it is fairly unknown that besides information about the general chemical constituents of a water, the classification reveals a wealth of information about at least of 44 other elements in a water. Mineral waters classified by Piper as “alkaline earth waters with higher alkaline content” usually have the relatively highest element concentrations (Section 11.6).

Surprisingly the concentration of rare earth elements characterize a mineral water more within a classification system than the concentrations of main constituents like Ca, K, Mg, or Na (Section 11.7). The highest loading elements on the first three PCs in the element matrix of German mineral waters are Cs, Dy, Er, Ge, Gd, Lu, Nd, Rb, Sm, Y, and Yb. Among the elements discriminating between stratigraphic, hydrogeological, and hydrogeochemical classes, Lu and Tm occur six times, Er, Dy, and Zr five times, Gd and Sm four times, Ca, Cs, Hf, Ho, Li, and Rb three times, Mg, Pr, Y, Yb, and Nd two times, and finally La, Na, and S only one time.

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12

CHARACTERIZATION OF BIOACTIVE COMPOUNDS IN FLAVORED WATERS AND FRUIT JUICES

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12.1 Introduction

National health authorities are facing increasing challenges due to shifts in population demographics (e.g., aging populations) and in lifestyle-related diseases. On the other hand, there is a growing awareness of the key role of foods (and beverages) in disease prevention and treatment. In fact, since proper nutrition affects health status and contributes to the prevention of many diseases, the various stakeholders have perceived the economic potential of functional food products (including beverages) as an important part of public health prevention strategies. Consequently, the production and consumption of functional foods has gained increased importance, as they provide a health benefit beyond the basic nutritional functions, leading to consumer demands.

The term "functional foods" was firstly used in Japan in the mid-1980s as "processed foods containing components that provide specific body functions"; such a demand arrived as an answer from the Japanese Ministry of Health & Welfare to improve the health of the aging Japanese population and reduce escalating health-care costs. In the United States, functional foods are defined as "foods and food components that provide a health benefit beyond basic nutrition," whereas in Europe a working definition of functional food is proposed as "a food that beneficially affects one or more target functions in the body beyond adequate nutritional effects in a way that is relevant to either an improved state of health and well-being and/or

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reduction of risk of disease, and it is consumed as part of a normal food pattern (not a pill, a capsule or any form of dietary supplement)" (Sun-Waterhouse, 2011).

In a regulatory sense, functional foods are not clearly classified and defined, although the details of the functionality (health or nutritional claims) should fulfill some basic requirements. In Europe, EC Regulation 1924/2006 regulates nutrition and health claims on "Nutrition and health claims made on foods." In the United States, functional foods also fall under the regulations for conventional foods: they must be safe to be marketed as foods, and the ingredients must be "generally recognized as safe" (GRAS) or approved as food additives (Corbo et al., 2014).

A large number of studies have been conducted in order to identify the physiologically active components in foods from all the edible sources that are believed to reduce the risks of several health problems. Fruits contain a wide range of health-promoting components, including dietary fiber, vitamins, and antioxidants. Among the latter, polyphenols have gained increasing interest due to their beneficial role against certain cancers, cardiovascular diseases, type-2 diabetes, obesity, and age-related macular degeneration (Corbo et al., 2014). Epidemiological studies suggest that regular or increased consumption of fruits may promote general health and well-being, as well as reduce the risk of chronic diseases, and that those health benefits can be obtained through a balanced fruit diet, or through the ingestion of foods containing fruit-derived ingredients. However, nowadays people do not consume sufficient amounts of fruits: for example, on average, an American consumer eats only about three servings of fruits and vegetables a day (Sun-Waterhouse, 2011). Therefore, introduction of different formats of fruit-derived foods and beverages can help to increase the total consumption of fruit components.

The most popular functional foods are those that are similar in appearance to a conventional food and possess validated physiological benefits beyond basic nutritional functions. Drinkable products are one of the most active functional food categories because of convenience, as well as the possibility to meet other consumer demands for container content, size, and appearance, as well as ease of distribution and storage for refrigerated and shelf-stable products (Corbo et al., 2014). Among the latter, convenience may be the most important attribute: a more mobile society, combined with busier lifestyles and changes in family demographics, led consumer's demand for ready-to-eat, easy-to-use products. Portable formulations such as on-the-run beverages are an effective answer. Given the fresh and healthy image of fruits to consumers, functional fruit juices or drinks including fruit components have been developed in many countries. Fruits used include cranberry, blueberry, apple, blackcurrant, acai, acerola, guarana, mango, bilberries, grapes, cherries, kiwifruits, strawberries, feijoa, peach, plums, cranberry, blueberry, and pomegranate (Sun-Waterhouse, 2011).

The functional benefits of a food product depend on the interactions between bioactive components and the food matrix, which can be exclusive, additive, or synergistic. Phytochemical components in whole foods provided increased effects in health compared to isolated individual phenolic phytochemicals, suggesting a synergistic interaction of these components with the food matrix. It is also possible to increase bioavailability through the design of synergistic interactions with polyphenols, in order to overcome the blood-brain barrier and digestion/absorption barriers, such as enzymatic and chemical modification in the human body (Scheepens et al., 2010). Apart from the beneficial health effects resulting from the incorporation of functional ingredients in food products, undesirable food attributes and technical issues may also occur, such as the increase in bitterness and astringency resulting from the inclusion of polyphenols in foods, due to the interaction between polyphenols, mainly procyanidins, and the glycoproteins in saliva (Sun-Waterhouse, 2011).

Fruit juices are subject to very detailed legislation guaranteeing their safety and quality. The Directive 2012/12/EU regulates the composition, manufacture, and labeling of fruit juices and certain similar products intended for human consumption. The text defines the composition of the various products that can be produced, including not only fruit juices, but also dehydrated fruit juice and fruit nectars. It also specifies the obligatory criteria for the various products, namely which fruits can be used, their minimum content, what ingredients can or cannot be added, and how these products must be designated on the label. As an example, it must be clearly indicated on the label when a product has been sweetened or when it has been obtained from concentrated juice.

Various types of flavored and/or nutrient-added water beverages are also present in the market. Some are simply bottled water with flavors added, whereas others may also contain other compounds such as vitamins, electrolytes, and amino acids. These additives must comply with all applicable safety requirements and must be identified in the ingredient list on the label. Food additives are substances added intentionally to foodstuffs to perform certain technological functions, for example, to color, to sweeten, or to help preserve foods. The European Union legislation defines them as “any substance not normally consumed as a food in itself and not normally used as a characteristic ingredient of food, whether or not it has nutritive value.” Once authorized, these substances are included in the EU list of permitted food additives laid down in Regulation EC 1333/2008, which also specifies their conditions of use, and were published in full in Regulation

EU 1129/2011. In addition, the list of flavorings authorized for use in foods in the EU (Regulation EU 872/2012) is also defined, bringing protection for consumers and clarity to the industry.

Fruit juice consumption has been showing a steady global rise (Borges et al., 2010). According to the Statistica Market Forecast, the total volumes of juices and nectars sold in EU in 2016 were 8088 million liters. The revenue in the “juices” segment in 2017 amounts to US$11,301 m in North America, with orange juice as the market’s large segment (US$4917 m). In Europe, other juice, juice mixtures, and smoothies stand for the largest share, with US$4516.6 m, with a total revenue of US$10,642 m.

The qualitative and quantitative analysis of bioactive composition is a requirement not only for product development, but also for quality control, in order to verify health content claims. Thus, it is imperative to analyze the composition and amounts of bioactive compounds before adding them to foods, after processing and during storage. The range of analytical methodologies available depends on the type of bioactive compounds under target.

Several analytical methods have been proposed for the quantification of the total antioxidant capacity (TAC) in biological and food samples. These methodologies are based on UV-Vis spectrometry, chemiluminescence, fluorimetry, electrochemistry, and chromatographic methods (Barroso et al., 2011a).

12.2 Bioactive Compounds in Juices and Flavored Waters

12.2.1 Phenolic Compounds

Dietary phenolics or polyphenols constitute one of the most abundant and widely distributed groups of natural products in the plant kingdom. More than 8000 phenolic structures are currently known. This class includes two subclasses of phenolic acids [hydroxybenzoic acids (C6–C1) and the hydroxycinnamic acids (C6–C3)], condensed and hydrolysable tannins, flavonoids, polyphenolic amides, stilbenes, volatile phenols, curcuminoids, coumarins, anthraquinones, lignins, etc. (Tsao, 2010). Flavonoids have a C6–C3–C6 skeleton. The aromatic ring A is derived from the acetate/malonate pathway, while ring B is derived from phenylalanine through the shikimate pathway. In plants, flavonoids may occur in several forms corresponding to additional modifications of the flavonoid backbone (e.g., hydroxylation, methylation, and glycosylation). Glycosylated forms usually occur as flavonoid *O*-glycosides and to a lesser extent as flavonoid *C*-glycosides and while the glycosidic O─C bond is acid labile, the C─C bond is acid-resistant.

Although any of the OH groups can be glycosylated, the 7-OH group in flavones and flavanones, the 3-OH and 7-OH in flavonols and flavan-3-ols, and the 3-OH and 5-OH in anthocyanidins are more common. *C*-Glycosylation has been found only at the C6 and/or C8 position for the flavonoid nucleus. With regard to the sugar moiety, the sugar most frequently found in association with flavonoids is glucose, but galactose, rhamnose, xylose, and arabinose are not uncommon, and mannose, fructose, and glucuronic and galacturonic acids are rare (Abad-García et al., 2009).

Several bioactivities have been attributed to phenolic compounds, namely, antioxidant, anti-allergenic, antiatherogenic, anti-inflammatory, anti-microbial, anti-thrombotic, cardioprotective, vasodilatory, and neuroprotective effects, among other (Balasundram et al., 2006).

12.2.1.1 Methodologies for the Determination of Phenolic Compounds

The Folin-Ciocalteu assay is the most commonly used spectrophotometric method to quantify the total phenolic content (TPC) of food extracts (Table 12.1). The assay is based on electron transfer reactions between the Folin-Ciocalteu reagent (composed of sodium tungstate, sodium molybdate, phosphoric acid, hydrochloric acid, lithium sulfate, and water) and phenolic compounds. The blue color developed during the redox reaction is proportional to the concentration of phenolic compounds, which can be spectrophotometrically determined around 765 nm. A calibration curve with gallic acid is usually performed and the results are expressed as gallic acid equivalents (GAE). However, the assay is not specific for TPC determinations. It is known that other types of compounds that may be present in high abundance in plant food extracts (ascorbic acid, dehydroascorbic acid, and reducing sugars (glucose and fructose)) can also reduce the Folin-Ciocalteu reagent, giving false results. Thus, different methodological approaches to improve the specificity of the Folin-Ciocalteu assay have been proposed, namely, (1) the partial purification of phenolics extracts using solid phase extraction (SPE) columns prior to the assay; (2) the calculation of a corrected TPC value by subtracting the ascorbic acid reducing activity from the TPC quantified in the plant food extract; or (3) the treatment of phenolic extracts with oxidative agents such as hydrogen peroxide at doses that oxidize the interfering compounds but not the compounds of interest (Sanchez-Rangel et al., 2013). Another method, the terbium-sensitized fluorescence method, which is based on fluorescence intensity measured at 545 nm upon excitation at 310 nm has shown $r = 0.99$ with the Folin-Ciocalteu method (Mahdavi et al., 2011).

Table 12.1 Chemical Composition of Fruit Juices

Common Name	Total Phenolic Content (Fluorescence or Spectrophotometry)	Total Antocyanin (TA) Content (Spectrophotometry)	Total Vitamin C Content (Titration or Spectrophotometry)	References
Apple	3.09 ± 0.08 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Apricot	2.73 ± 0.02 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Banana	120.37 ± 0.85 μg GAE/g sample[b]	–	72.50 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Bilimbi	251.83 ± 0.79 μg GAE/g sample[b]	–	154.14 ± 6.44 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Calamansi	453.47 ± 1.38 μg GAE/g sample[b]	–	227.20 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Carrot	236.02 ± 0.57 μg GAE/g sample[b]	–	63.04 ± 1.49 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Cashew apple	1.29 ± 0.15 mg GAE/g[b]	–	1.37 ± 0.06 mg AAE/g[d]	Rodríguez et al. (2017)
Celery	200.99 ± 0.34 μg GAE/g sample[b]	–	56.60 ± 0.74 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Ciruela	55.0 ± 2.1 mg GAE/100 g[b]	1.35 ± 0.04 mg TA/100 g	29.6 ± 0.9 mgAAE/100 g[c]	Almeida et al. (2011)
Coconut	71.85 ± 7.84 μg GAE/g sample[b]	–	51.87 ± 0.74 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Dokong	386.82 ± 5.53 μg GAE/g sample[b]	–	87.54 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Gandaria	372.35 ± 1.43 μg GAE/g sample[b]	–	156.29 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Grapefruit	4.30 ± 0.06 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Guava	857.24 ± 12.65 μg GAE/g sample[b]	–	590.31 ± 7.44 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Hippo apple	790.40 ± 0.23 μg GAE/g sample[b]	–	108.16 ± 1.49 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Indian gooseberry	204.75 ± 4.99 μg GAE/g sample[b]	–	102.58 ± 6.44 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Indian jujube	396.96 ± 7.77 μg GAE/g sample[b]	–	84.10 ± 2.68 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Jackfruit	319.01 ± 1.02 μg GAE/g sample[b]	–	72.50 ± 1.97 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
	29.0 ± 0.63 mg GAE/100 g[b]	0.46 ± 0.0 mg TA/100 g	1.2 ± 0.0 mgAAE/100 g[c]	Almeida et al. (2011)
Jentik	417.14 ± 3.41 μg GAE/g sample[b]	–	149.85 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Lime	463.08 ± 8.48 μg GAE/g sample[b]	–	259.42 ± 7.44 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Longan	399.13 ± 5.15 μg GAE/g sample[b]	–	380.61 ± 1.49 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Malabar tamarind	117.28 ± 0.40 μg GAE/g sample[b]	–	280.91 ± 7.44 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Malay apple	81.51 ± 0.06 μg GAE/g sample[b]	–	100.43 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Mangaba	98.8 ± 5.6 mg GAE/100 g[b]	0.79 ± 0.04 mg TA/100 g	96.3 ± 1.7 mgAAE/100 g[c]	Almeida et al. (2011)
Mango	79.72 ± 2.77 μg GAE/g sample[b]	–	121.06 ± 1.28 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
	6.04 ± 0.12 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Mangosteen	647.59 ± 9.52 μg GAE/g sample[b]	–	66.91 ± 3.24 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Melon	162.72 ± 0.81 μg GAE/g sample[b]	–	74.64 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)

Murici	159.9 ± 5.6 mg GAE/100 g[b]	1.02 ± 0.00 mg TA/100 g	11.8 ± 0.0 mgAAE/100 g[c]	Almeida et al. (2011)
Nam nam	52.59 ± 0.53 μg GAE/g sample[b]	–	106.01 ± 3.24 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Nutmeg	658.76 ± 4.04 μg GAE/g sample[b]	–	139.10 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Orange	4.08 ± 0.05 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Papaya	377.43 ± 1.10 μg GAE/g sample[a]	–	268.02 ± 7.44 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
	53.2 ± 3.6 mg GAE/100 g[b]	0.69 ± 0.04 mg TA/100 g	8.6 ± 0.0 mg AAE/100 g[c]	Almeida et al. (2011)
Peach	6.36 ± 0.60 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Pineapple	359.28 ± 2.53 μg GAE/g sample[b]	–	78.94 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
	38.1 ± 0.7 mg GAE/100 g[b]	0.32 ± 0.15 mg TA/100 g	13.0 ± 0.9 mg AAE/100 g[c]	Almeida et al. (2011)
	1.06 ± 0.08 mg QE/100 g[a]	–	–	Mahdavi et al. (2011)
Pomegranate	243.89 mg GAE/100 mL juice[b]	[e]	–	González-Molina et al. (2009)
	9.10 ± 0.16 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Pommelo	606.50 ± 0.22 μg GAE/g sample[b]	–	285.21 ± 7.44 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Pulasan	199.07 ± 2.18 μg GAE/g sample[b]	–	65.62 ± 1.49 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Rambai	149.49 ± 3.06 μg GAE/g sample[b]	–	67.34 ± 0.74 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Rambutan	223.75 ± 0.57 μg GAE/g sample[b]	–	60.89 ± 0.74 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Red grape	6.69 ± 0.06 mg QE/mL[a]	–	–	Mahdavi et al. (2011)
Santol, kechapi	617.04 ± 2.23 μg GAE/g sample (mature flesh)[b]	–	98.28 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
	60.96 ± 1.44 μg GAE/g sample (ripe aril)[b]	–	120.19 ± 1.97 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Sapodilla	255.88 ± 0.91 μg GAE/g sample[b]	–	72.50 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
	13.5 ± 1.1 mg GAE/100 g[b]	0.46 ± 0.07 mg TA/100 g	3.9 ± 0.0 mg AAE/100 g[c]	Almeida et al. (2011)
Snake fruit	177.99 ± 0.94 μg GAE/g sample[b]	–	98.28 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Sour cherry	10.14 ± 0.07 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Soursop	185.80 ± 0.59 μg GAE/g sample[b]	–	104.72 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
	54.8 ± 2.7 mg GAE/100 g[b]	0.19 ± 0.03 mg TA/100 g	3.3 ± 0.9 mg AAE/100 g[c]	Almeida et al. (2011)
Star fruit	699.67 ± 2.24 μg GAE/g sample[b]	–	85.39 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Strawberry	7.39 ± 0.16 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)
Sugar cane	116.55 ± 0.30 μg GAE/g sample[b]	–	79.80 ± 1.49 μg AAE/g sample[c]	Sulaiman and Ooi (2014)

Continued

Table 12.1 Chemical Composition of Fruit Juices—cont'd

Common Name	Total Phenolic Content (Fluorescence or Spectrophotometry)	Total Antocyanin (TA) Content (Spectrophotometry)	Total Vitamin C Content (Titration or Spectrophotometry)	References
Sweetsop,	134.35 ± 1.43 μg GAE/g sample[b]	–	98.28 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
sugar-apple	81.7 ± 4.0 mg GAE/100 g[b]	0.73 ± 0.18 mg TA/100 g	29.6 ± 0.9 mg AAE/100 g[c]	Almeida et al. (2011)
Tamarind	83.8 ± 6.1 mg GAE/100 g[b]	3.16 ± 0.40 mg TA/100 g	3.1 ± 0.9 mg AAE/100 g[c]	Almeida et al. (2011)
Umbu	44.6 ± 2.7 mg GAE/100 g[b]	0.46 ± 0.00 mg TA/100 g	12.1 ± 0.4 mg AAE/100 g[c]	Almeida et al. (2011)
Watermelon	104.97 ± 0.19 μg GAE/g sample[b]	–	61.75 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Wax apple	374.83 ± 4.03 μg GAE/g sample[b]	–	72.50 ± 3.72 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
Wild mango	421.64 ± 0.32 μg GAE/g sample[b]	–	396.93 ± 3.94 μg AAE/g sample[c]	Sulaiman and Ooi (2014)
White grape	2.85 ± 0.04 mg QE/100 mL[a]	–	–	Mahdavi et al. (2011)

[a] Terbium sensitized fluorescence method with $r = 0.9906$ with Folin-Ciocalteu method.
[b] Folin-Ciocalteu method.
[c] Titration.
[d] Spectrophotometric method.
[e] Anthocyanins were quantified by HPLC-DAD: 21.5 mg TA/100 mL juice.

Total flavonoid content (TFC) is assessed by a complexation reaction of unsubstituted catechol groups with aluminum chloride ($AlCl_3$, 2%–10%). The solution is added to a sample and can be applied in the presence of acid, acetate solution, methanol, or water. TFC is determined spectrophotometrically in the range of 410–430 nm. Additionally, another method is based on the complexation reaction carried out in the presence of $NaNO_2$ in alkaline medium (NaOH). In this case, the method is based on the nitration of any aromatic ring bearing catechol group with its three or four positions unsubstituted or not sterically blocked. After addition of Al^{3+}, a yellow solution is formed, which then turned immediately to red after the addition of NaOH, and the value of absorbance is measured at $\lambda = 510$ nm. A standard curve performed with quercetin is usually performed (Pękal and Pyrzynska, 2014).

Total anthocyanin content can also be determined by spectrophotometry. The method is based on the reversible structural transformations of anthocyanins as a function of the pH, which is then reflected in different absorbance spectra. The colored oxonium form predominates at pH 1.0 and the colorless hemiketal form at pH 4.5. Therefore, absorbance is measured at 510 nm (the absorption maximum of anthocyanins) and 700 nm (for blank correction) using buffer solutions at these two pH values (Giusti and Wrolstad, 2001). Other authors directly measured anthocyanins diluted in ethanol-1.5 N hydrochloric acid (85:15) at 535 nm (Table 12.1; Almeida et al., 2011).

In order to determine the phenolic profile, it is necessary to use chromatographic methods (Table 12.2). The analysis of phenolic compounds by high-performance liquid chromatography (HPLC) coupled to diode array detection (DAD)/photodiode array detection (PAD) is possible due to the characteristic UV/vis spectra of phenolic compounds in the range of 200–600 nm. Hydroxybenzoic acids (e.g., gallic, *p*-hydroxybenzoic, protocatechuic, vanillic, and syringic acids) are characterized by a maximum absorption band at 240–280 nm. Protocatechuic acid, a dihydroxybenzoic acid, possesses two maxima. The hydroxycinnamic acids (e.g., caffeic, ferulic, *p*-coumaric, and sinapic acids) show two peaks at 225–235 nm and 290–330 nm, respectively. The UV spectra of flavonoids are characterized by two bands: the longer wavelength absorption band is called band I and the shorter one is band II (Bohm, 1999). Typically, flavones (e.g., apigenin, luteolin) exhibit their maximum at 250–270 nm (Band II) and 330–350 nm (Band I), flavonols (e.g., quercetin, kaempferol, myricetin) at 250–270 nm (Band II) and 330–380 nm (Band I), flavan-3-ols (catechins) and proanthocyanidins (procyanidins) at 270–280 nm (Band II), flavanones (e.g., hesperetin) and dihydroflavonols (e.g., taxifolin) at 280–290 nm (Band II) and 300–330 nm (shoulder, sh) (Band I), isoflavones (e.g., genistein, daidzein) at 255–265 nm (Band II) and 300–330 nm (sh) (Band I), chalcones at 240–270 nm (low intensity)

Table 12.2 Phenolic Compounds Quantified in Fruit Juices by Liquid Chromatography Including a Brief Description of Sample Preparation and Chromatographic Analysis

Beverage	Compound	Concentration (mg/L)	Sample Preparation	Chromatographic Analysis	References
Star fruit juice	(−)Epicatechin	73.1	SPE 3 mL end-capped C18 column (Isolute)	HPLC-DAD Column: Shim-Pack VP-ODS (250 mm × 4.6 mm) Mobile phase: 2% (v/v) acetic acid/acetonitrile (95:5, v/v), 0.8 mL/min, at 40°C $V_{inj} = 20\ \mu L$	Shui and Leong (2004)
	Gallic acid	19.5			
Hippo apple	Ellagic acid	1269.48 ± 33.82[a]	Filtration (0.2 μm); 5 mL of juice hydrolyzed with 10 mL of 2 M HCl, 40 min in boiling water	UPLC-PAD Column: Acquity UPLC BEH C_{18} 1.7 μm (100 mm × 2.1 mm i.d.) Mobile phase: A (1% acetic acid) and B (acetonitrile); gradient mode; 0.2 mL/min $V_{inj} = 5.0\ \mu L$ $\lambda_{det} = 350\ nm$	Sulaiman and Ooi (2014)
	Myricetin	265.57 ± 2.45[a]			
	Quercetin	61.70 ± 1.97[a]			
Indian gooseberry	Gallic acid	230.69 ± 3.31[a]			
	Dehydroquercetin	103.33 ± 9.31[a]			
	Myricetin	85.42 ± 6.51[a]			
	Quercetin	142.68 ± 12.49[a]			
	Kaempferol	4.54 ± 0.19[a]			
Orange juice	*Flavanones*		10 mL of each sample were centrifuged (4500 *g*, 10 min); the supernatant and pellet were separated The supernatant was filtered (0.45 μm PVDF) The pellet was extracted with 500 μL of DMSO and filtered (0.45 μm PVDF)	UHPLC-MS/MS (QqQ) Column: ACQUITY BEH C18 (150 × 2.1 mm, 1.7 μm; waters) Mobile phase: water/formic acid (99.9:0.1, v/v) (A) and acetonitrile/formic acid (99.9:0.1, v/v) (B); gradient mode; 0.32 mL/min $V_{inj} = 10\ \mu L$ Negative mode MRM mode	Escudero-López et al. (2016)
	Naringenin-7-*O*-rutinoside	400.9 ± 24.8			
	Hesperetin-7-*O*-rutinoside	304.1 ± 13.2			
	Naringenin-7-*O*-glucoside	0.7 ± 0.1			
	Hesperetin-7-*O*-glucoside	13.1 ± 2.1			
	Isosakuranetin-7-*O*-rutinoside	43.3 ± 9.8			
	Naringenin	0.2 ± 0.0			
	Homoeriodictyol	N.Q.			
	Hesperetin	0.1 ± 0.0			
	Isosakuranetin	N.Q.			

Lemon juice	*Flavanones and flavones*		Samples were centrifuged (10,500 rpm, 5 min) and the supernatant was filtered (0.45 μm PVDF)	HPLC-DAD Column: Lichrocart RP-18 (250 mm × 4 mm, 5 μm) Mobile phase: 5% formic acid (v/v) (A); HPLC-grade methanol (B); gradient mode; 1 mL/min $V_{inj} = 20\ \mu L$ $\lambda_{det} = 280, 320, 360$, and 520 nm	González-Molina et al. (2012)
	Eriocitrin	62.6 ± 0.6			
	Hesperidin	61.4 ± 0.9			
	Vicenin-2	6.6 ± 0.4			
	Diosmetin-6,8-di-*C*-glucoside	56.6 ± 0.8			
	Diosmin	<2.5			
Elderberry juice	*Anthocyanins*				
	Cyanidin 3,5-di-*O*-glucoside + cyanidin 3-*O*-sambubioside-5-*O*-glucoside	33.6 ± 1.7			
	Cyanidin 3-*O*-sambubioside + cyanidin 3-*O*-glucoside	335.4 ± 2.9			
Grape juice	*Anthocyanins*				
	Delphinidin 3-*O*-glucoside	8.4 ± 1.1			
	Cyanidin 3-*O*-glucoside	N.Q.			
	Petunidin 3-*O*-glucoside	6.5 ± 0.5			
	Peonidin 3-*O*-glucoside	12.0 ± 0.7			
	Malvidin 3-*O*-glucoside	23.4 ± 1.2			
Pumpkin juice	β-Carotene	1.0[b]	According to Bhosale et al. (2004)	HPLC Column: C18 Hypersil GOLD (100 × 2.1 mm, 1.9 μm, ThermoFisher) Mobile phase: acetonitrile:2-propanol:ethyl acetate (50:40:10 v/v), at 0.7 mL/min $\lambda_{det} = 450$ nm	AlJahani and Cheikhousman (2017) Bhosale et al. (2004)

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Table 12.2 Phenolic Compounds Quantified in Fruit Juices by Liquid Chromatography Including a Brief Description of Sample Preparation and Chromatographic Analysis—cont'd

Beverage	Compound	Concentration (mg/L)	Sample Preparation	Chromatographic Analysis	References
Tomato juice	*Carotenoids*		According to Sánchez-Moreno et al. (2003)	HPLC-PAD Column: C18 Hypersil ODS (250 × 4.6 mm, 5 μm) Mobile phase: acetonitrile (A), methanol (B), dichloromethane (C) and hexane (D); gradient mode; 0.8 mL/min $V_{inj} = 20\ \mu L$ $\lambda_{det} = 470\ nm$	Sánchez-Moreno et al. (2003), Sánchez-Moreno et al. (2006)
Freshly made	Lutein	29.4 ± 4.3[c]			
	Lycopene epoxide	53.2 ± 5.02[c]			
	Lycopene	1024 ± 98.3[c]			
	γ-Carotene	48.3 ± 4.23[c]			
	β-Carotene	369 ± 20.0[c]			
Commercial pasteurized (6 samples)	Lutein	33.6 ± 1.96–70.6 ± 10.09[c]			
	Lycopene epoxide	78.7 ± 4.30–183 ± 23.0[c]			
	Lycopene	2129 ± 270–3435 ± 226[c]			
	γ-Carotene	56.4 ± 5.95–115 ± 5.47[c]			
	β-Carotene	182 ± 8.79–321 ± 14.4[c]			

Cornelian cherry	Caffeic acid	n.d.	Juices were filtered (0.45 μm)	HPLC-DAD Column: Lichrospher RP 18-5 (250 × 4.6 mm, 5 μm, Hichrom) Mobile phase: 5% (v/v) formic acid (A), and 95% (v/v) acetonitrile (B); gradient mode; 0.8 mL/min; 25°C. $V_{inj} = 50\ \mu L$ $\lambda_{det} = 520\ nm$ Anthocyanin contents were expressed as mg of cyanidin-3-glucoside per L of sample	Antolak et al. (2017)
	Cinnamic acid	0.143 ± 0.011			
	Gallic acid	2.025 ± 0.314			
	Protocatechuic acid	0.379 ± 0.271			
	p-Coumaric acid	0.108 ± 0.048			
	Rosmarinic acid	0.128 ± 0.062			
	4-Hydroxybenzoic acid	n.d.			
	Catechin	n.d.			
	Epicatechin	n.d.			
	Quercetin-3-*O*-rutinoside	n.d.			
	Delphinidin-3-*O*-glucoside	n.d.			
	Cyanidin-3-*O*-sambubioside-5-*O*-glucoside	n.d.			
	Cyanidin-3-*O*-glucoside	0.280 ± 0.039			
	Cyanidin-3-*O*-sambubioside	n.d.			
	Cyanidin-3-*O*-robinobioside	0.321 ± 0.041			
	Petunidin-3-*O*-galactoside	n.d.			
	Petunidin-3-*O*-glucoside	n.d.			
	Pelargonidin-3-*O*-glucoside	0.380 ± 0.052			
	Pelargonidin-3-*O*-rutinoside	n.d.			
	Pelargonidin-3-*O*-robinobioside	0.302 ± 0.022			

Continued

Table 12.2 Phenolic Compounds Quantified in Fruit Juices by Liquid Chromatography Including a Brief Description of Sample Preparation and Chromatographic Analysis—cont'd

Beverage	Compound	Concentration (mg/L)	Sample Preparation	Chromatographic Analysis	References
Lingonberry	Caffeic acid	n.d.			
	Cinnamic acid	0.191 ± 0.014			
	Gallic acid	0.071 ± 0.009			
	Protocatechuic acid	0.497 ± 0.087			
	p-Coumaric acid	0.179 ± 0.052			
	Rosmarinic acid	0.128 ± 0.037			
	4-Hydroxybenzoic acid	0.150 ± 0.074			
	Catechin	0.662 ± 0.121			
	Epicatechin	0.304 ± 0.082			
	Quercetin-3-*O*-rutinoside	n.d.			
	Delphinidin-3-*O*-glucoside	n.d.			
	Cyanidin-3-*O*-sambubioside-5-*O*-glucoside	n.d.			
	Cyanidin-3-*O*-glucoside	0.605 ± 0.054			
	Cyanidin-3-*O*-sambubioside	n.d.			
	Cyanidin-3-*O*-robinobioside	n.d.			
	Petunidin-3-*O*-galactoside	0.320 ± 0.057			
	Petunidin-3-*O*-glucoside	0.528 ± 0.052			
	Pelargonidin-3-*O*-glucoside	0.359 ± 0.063			
	Pelargonidin-3-*O*-rutinoside	0.344 ± 0.074			
	Pelargonidin-3-*O*-robinobioside	n.d.			

Elderberry	Caffeic acid	2.603 ± 0.313			
	Cinnamic acid	n.d.			
	Gallic acid	0.286 ± 0.082			
	Protocatechuic acid	0.550 ± 0.057			
	p-Coumaric acid	n.d.			
	Rosmarinic acid	0.128 ± 0.019			
	4-Hydroxybenzoic acid	0.265 ± 0.096			
	Catechin	0.918 ± 0.107			
	Epicatechin	n.d.			
	Quercetin-3-*O*-rutinoside	1.321 ± 0.307			
	Delphinidin-3-*O*-glucoside	2.057 ± 0.371			
	Cyanidin-3-*O*-sambubioside-5-*O*-glucoside	2.260 ± 0.219			
	Cyanidin-3-*O*-glucoside	3.738 ± 0.147			
	Cyanidin-3-*O*-sambubioside	3.143 ± 0.262			
	Cyanidin-3-*O*-robinobioside	n.d.			
	Petunidin-3-*O*-galactoside	n.d.			
	Petunidin-3-*O*-glucoside	n.d.			
	Pelargonidin-3-*O*-glucoside	n.d.			
	Pelargonidin-3-*O*-rutinoside	n.d.			
	Pelargonidin-3-*O*-robinobioside	n.d.			
Grape juice: purple grape juices (*n* = 4)	Cyanidin-3-*O*-glucoside Delphinidin-3-*O*-glucoside Peonidin-3-*O*-glucoside Malvidin-3-*O*-glucoside	0.76 ± 0.04–20.91 ± 0.83 4.10 ± 0.40–49.51 ± 1.80 8.59 ± 0.82–32.60 ± 1.78 95.26 ± 1.95–425.96 ± 6.36	Filtration (0.20 μm)	HPLC-DAD Column: C18-ODS (150 × 4 mm, 5 μm) Mobile phase: ultra-pure water, formic acid, acetonitrile (87:10:3 v/v/v) (A), and ultra-pure water, formic acid, acetonitrile (40:10:50 v/v/v) (B), 0.8 mL/min, at 25°C $V_{inj} = 50\ \mu L$ $\lambda_{det} = 518\ nm$	Dani et al. (2007)

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Table 12.2 Phenolic Compounds Quantified in Fruit Juices by Liquid Chromatography Including a Brief Description of Sample Preparation and Chromatographic Analysis—cont'd

Beverage	Compound	Concentration (mg/L)	Sample Preparation	Chromatographic Analysis	References
Grape juice: white and purple grape juices, $n=8$)	(+)Catechin (−)Epicatechin	0.38 ± 0.02–86.43 ± 2.31 0.92 ± 0.16–22.13 ± 1.92	Filtration (0.20 µm)	HPLC-DAD Column: C18-ODS (150 × 4 mm, 5 µm) Mobile phase: ammonium hydroxide diphosphate 50 mM, pH 2.6) (A), 20% of solvent A and 80% of acetonitrile (B), orthophosphoric acid 0.2 M, pH 1.5), 0.5 mL/min, 40°C $V_{\mathrm{inj}} = 5\,\mu\mathrm{L}$ $\lambda_{\mathrm{det}} = 204\,\mathrm{nm}$	Dani et al. (2007)
Goldenberry juice (freeze-dried powder)	Chlorogenic acid	1.2746 ± 0.015[a]	0.1 g of freeze-dried goldenberry juice in 5.9 mL methanol (vortex, 1 min). Centrifuged at 1222 *g*, 5 min. The supernatant was filtered (0.45 µm cellulose acetate filter)	LC/MS/MS (Triple Quadrupole, ESI) Column: Zorbax SB-C18 (2.1 × 50 mm, 1.8 µm) Mobile phase: 0.05 mL formic acid in 100 mL distilled water and 5 mM ammonium formate (A), and methanol (B), 0.5 mL/min, 35°C $V_{\mathrm{inj}} = 5\,\mu\mathrm{L}$ Negative mode	Dag et al. (2017)
	p-Coumaric acid	0.4314 ± 0.0008[a]			
	Ferulic acid	0.3712 ± 0.019			
	Gallic acid	≤0.3			
	Caffeic acid	≤0.3			
	Quercetin	≤0.3			
	Myricetin	≤0.15			
	Kaempferol	≤0.15			
Lemon juice	*Flavonols glycosides* Quercetin 3-*O*-rutinoside- 7-*O*-hexoside Quercetin 3-*O*-rutinoside *Flavones glycosides* Apigenin 6,8-di-*C*-glucoside Diosmetin 6,8-di-*C*-glucoside Diosmetin 7-*O*-rutinoside *Flavanones glycosides* Eriodictyol 7-*O*-rutinoside Hesperetin 7-*O*-rutinoside	 0.19 ± 0.01[b] 0.61 ± 0.01[b] 0.64 ± 0.01[b] 5.35 ± 0.09[b] 2.39 ± 0.04[b] 2.91 ± 0.05[b] 3.11 ± 0.06[b]	Samples were centrifuged (12,000 rpm, 5 min) and filtered through a PVDF filter (0.22 µm)	HPLC-DAD-ESI/MS^n Column: Luna C18 (250 × 4.6 mm, 5 µm) Mobile phase: Water:formic acid (99:1, v/v) (A) and acetonitrile (B); 1 mL/min; gradient mode Positive ionization mode for anthocyanins Negative ionization mode for other flavonoids $V_{\mathrm{inj}} = 30\,\mu\mathrm{L}$ $\lambda_{\mathrm{det}} = 280$ and 360 nm for all flavonoids	Gironés-Vilaplana et al. (2015)

Papaya in 5% in citric acid solution	*Xanthones glycosides* Mangiferin Mangiferin gallate Isomangiferin gallate *Flavonols glycosides* Quercetin 3-*O*-rutinoside Quercetin 3-*O*-galactoside Quercetin 3-*O*-glucoside	0.28 ± 0.01[b] 0.08 ± 0.00[b] 0.25 ± 0.02[b] 0.18 ± 0.01[b] 0.06 ± 0.00[b] 0.07 ± 0.00[b]			
Noni 5% in citric acid solution	*Flavonols glycosides* Quercetin 3-*O*-rutinoside-7-*O*-pentoside Quercetin 3-*O*-rutinoside Kaempferol 3-*O*-rutinoside *Anthraquinone* Lucidin	0.13 ± 0.00[b] 0.98 ± 0.02[b] 0.06 ± 0.01[b] 2.06 ± 0.08[b]			
Black chokeberry	*Anthocyanins (520 nm)* Cyanidin-3-*O*-galactoside Cyanidin-3-*O*-glucoside Cyanidin-3-*O*-arabinoside Cyanidin-3-*O*-xyloside *Flavonols* (360 nm) Quercetin diglucoside Quercetin pentosilhexoside Quercetin 3-*O*-rhamnosyl-galactoside Quercetin 3-*O*-galactoside Quercetin 3-*O*-glucoside *Hydroxycinnamic acid derivatives* 3-*O*-caffeoylquinic acid	40.84 ± 0.04[b] 1.87 ± 0.00[b] 16.51 ± 0.01[b] 2.03 ± 0.01[b] 2.31 ± 0.06[b] 3.34 ± 0.20[b] 5.69 ± 0.19[b] 6.76 ± 0.69[b] 3.73 ± 0.29[b] 12.47 ± 0.24[b]	Samples were centrifuged (12,000 rpm, 5 min) and filtered through a PVDF filter (0.22 μm)	HPLC-DAD-ESI/MS^n Column: Luna C18 (250 × 4.6 mm, 5 μm) Mobile phase: Water:formic acid (99:1, v/v) (A) and acetonitrile (B); 1 mL/min; gradient mode Positive ionization mode for anthocyanins Negative ionization mode for other flavonoids $V_{inj} = 30\ \mu L$ $\lambda_{det} = 280, 320, 360,$ and 520 nm	Gironés-Vilaplana et al. (2012a)

Continued

Table 12.2 Phenolic Compounds Quantified in Fruit Juices by Liquid Chromatography Including a Brief Description of Sample Preparation and Chromatographic Analysis—cont'd

Beverage	Compound	Concentration (mg/L)	Sample Preparation	Chromatographic Analysis	References
Aronia-citrus	*Flavanones*				González-Molina et al.
juice	Eriocitrin	11.45 ± 0.08			(2008)
	Hesperetin	13.54 ± 0.14			
	Flavones	7.75 ± 0.19			
	Diosmetin-6,8-di-*O*-	<0.25			
	glucoside	0.59 ± 0.02			
	Diosmin	1.31 ± 0.02			
	Vicenin-2	9.19 ± 0.20			
	Anthocyanins	15.08 ± 0.10			
	Cyanidin-3-*O*-glucoside	1.11 ± 0.03			
	Cyanidin-3-*O*-arabinoside	19.72 ± 0.17			
	Cyanidin-3-*O*-galactoside	14.69 ± 0.13			
	Cyanidin-3-*O*-xyloside	4.31 ± 0.13			
	Hydroxycinnamic acids				
	3-*O*-caffeoylquinic acid				
	5-*O*-caffeoylquinic acid				
	Σ Quercetin derivatives				
Pulp and			For resveratrol:	HPLC-UV–Vis	Silva et al. (2014)
by-products of	Resveratrol	25.67 ± 0.67[d]	Freeze-dried samples	Column: Nova Pack C18 (CLC-ODS,	
tropical fruits	Coumarin	102.49 ± 4.26[d]	(5 g) in 60 mL of	4.6 × 250 mm, 3 μm)	
Guava	Resveratrol	112.51 ± 2.01[d]	ethanol:water (1:1),	For resveratrol:	
by-product	Coumarin	71.18 ± 6.84[d]	heated for 30 min at	Mobile phase: water pH 2.9 using H_3PO_4)	
Surinam cherry	Coumarin	60.28 ± 6.04[d]	70°C	(A) and acetonitrile (B), 75A:25B, isocratic,	
by-product	Coumarin	57.39 ± 6.13[d]	Filtration (Whatman	1.2 mL/min, 40°C	
Passion fruit			No. 1), evaporation	$V_{inj} = 100\ \mu L$	
by-product			under vacuum at 70°C.	$\lambda_{det} = 306$ nm	
Mango pulp			Resuspension in 5 mL	For Coumarin: Mobile phase: water (A) and	
			methanol	methanol (B), 60A:40B, isocratic, 1.0 mL/min	
			For Coumarin:, 1 g of	40°C	
			freeze-dried sample in	$V_{inj} = 100\ \mu L$	
			10 mL of ethanol:water	$\lambda_{det} = 274$ nm	
			(1:1), maceration		
			for 24 h. Filtration		
			(Whatman No. 1)		

Table 12.2 Phenolic Compounds Quantified in Fruit Juices by Liquid Chromatography Including a Brief Description of Sample Preparation and Chromatographic Analysis—cont'd

Beverage	Compound	Concentration (mg/L)	Sample Preparation	Chromatographic Analysis	References
Commercial orange juice (7 samples)	*Carotenoids*		Extraction with THF containing 0.1 g/L BHT (More details in Sánchez-Moreno et al. (2003))	HPLC-PAD Column: C-18 Hypersil ODS (250 × 4.6 mm, 5 μm) Mobile phase: methanol/water (75:25) (A) and acetonitrile/dichloromethane/methanol (70:20:10) (B), gradient mode, 1.0 mL/min $V_{inj} = 20\ \mu L$ $\lambda_{det} = 450\ nm$	Sánchez-Moreno et al. (2003)
	β-Cryptoxanthin	1.49 ± 0.16–2.66 ± 0.60			
	α-Cryptoxanthin	0.20 ± 0.00–1.30 ± 0.07			
	Zeaxanthin	0.12 ± 0.02–1.31 ± 0.14			
	Lutein	0.65 ± 0.07–2.91 ± 0.64			
	β-Carotene	0.21 ± 0.00–0.77 ± 0.08			
	α-Carotene	0.14 ± 0.00–0.14 ± 0.00			
	Flavanones		50 mL of 80% aqueous methanol (100 μg of BHT) added to 30 mL of sample; ultrasonicated for 5 min. 20 mL of 6 M HCl were added (90°C, 2 h). The sample was cooled, made up to 100 mL with methanol, and ultrasonicated for 5 min. Filtration through a 0.45 μm membrane filter	HPLC-PAD Column: C-18 Hypersil ODS (250 × 4.6 mm, 5 μm) Mobile phase: water pH 2.5 with a 50 mM H_3PO_4 (A) and acetonitrile (B), gradient mode, 1.0 mL/min $V_{inj} = 20\ \mu L$ $\lambda_{det} = 280\ nm$	
	Naringenin	4.92 ± 2.4–36.54 ± 4.4			
	Hesperetin	31.23 ± 0.8–100.52 ± 10.9			

Continued

Table 12.2 Phenolic Compounds Quantified in Fruit Juices by Liquid Chromatography Including a Brief Description of Sample Preparation and Chromatographic Analysis—cont'd

Beverage	Compound	Concentration (mg/L)	Sample Preparation	Chromatographic Analysis	References
Butiá nectar	Caffeic acid	15.0 ± 0.9[e]	Samples were filtered through a 0.22 μm nylon membrane filter	UFLC-PDA-ESI-TOF/MS Column: Luna C18 (2.0 × 150 mm, 100 Å, 3 μm) Mobile phase: 0.1% aqueous formic acid pH 2.8 (A) and acetonitrile (B), gradient mode, 0.2 mL/min Negative ionization mode $V_{inj} = 20\ \mu L$	Hoffmann et al. (2017)
	Chlorogenic acid	37.7 ± 0.6[e]			
	p-Coumaric acid	5.0 ± 0.6[e]			
	Ferulic acid	6.6 ± 0.9[e]			
	Gallic acid	5.3 ± 0.1[e]			
	Hydroxybenzoic acid	23.4 ± 1.7[e]			
	Vanilic acid	2.4 ± 0.4[e]			
	(+)-Catechin	70.2 ± 1.3[e]			
	(−)-Epicatechin	212.0 ± 8.6[e]			
	Hesperetin	14.2 ± 5.1[e]			
	Pinocembrin	0.7 ± 0.3[e]			
	Quercetin	8.0 ± 1.1[e]			
	Quercetin-3-*O*-rutinoside	60.8 ± 3.8[e]			

[a] mg/100 g.
[b] mg/100 mL.
[c] μg/100 mL.
[d] mg/100 g dry basis.
[e] μg/100 g.
n.d., not detected; *N.Q.*, not quantified; *MRM*, multiple reaction monitoring mode.

(Band II) and 340–390 nm (Band I), aurones at 240–270 nm (low intensity) (Band II) and 390–430 nm (Band I), and anthocyanins and anthocyanidins (e.g., pelargonidin, cyanidin, delphinidin) at 270–280 nm (Band II) and 500–530 nm (Band I) (Markham, 1982; Bohm, 1999).

The exact wavelength and magnitude of each band depend on several factors, such as the nature of the C-ring, the point of attachment of the B-ring to the C-ring, and the nature of the substituents at the A- and B-rings. Bands I and II usually reflect B-ring and A-ring substitutions, respectively. Thus, increasing the hydroxylation of the A-ring induces a notable bathochromic shift (to higher wavelengths) in Band II and a smaller effect on Band I, while increasing the oxygenation of the B-ring produces a bathochromic shift in Band I and although it does not produce a shift in Band II, this band may appear as either one or two peaks depending on the B-ring oxidation pattern (Mabry et al., 1970). On the other hand, if those positions lack OH groups or are substituted by *O*-alkyl or *O*-sugar groups, a hypsochromic shift (displacement to lower wavelength) usually occurs compared to the corresponding aglycone. Acyl substituents cause an additional maximum in the UV spectrum of flavonoid glycosides. For example, a coumaroyl substituent (a conjugated system) produced an extra absorption maximum at around 310–320 nm in the UV spectrum (Mabry et al., 1970; Bohm, 1999).

Routine HPLC methods use reverse-phase octadecyl silica (C18) columns for phenolic compounds (Table 12.2), although other types of columns can also be used, such as C12, C8 (Robards, 2003; Kumar, 2017), and C6 phenyl columns (Borges et al., 2010).

The use of a UV or DAD detector does not allow the identification of the sugar component of a glycoside, but it is possible to ascertain chromatographically the level of glycosylation by the retention time recorded and the shape of spectra. The mass spectrometer achieves very high sensitivity and provides information on the molecular mass and on structural features of phenolic compounds. With regard to the structure characterization of polyphenols, information can be obtained on (1) the aglycone moiety, (2) the types of carbohydrates (mono-, di-, tri-, or tetrasaccharides and hexoses, desoxyhexoses, or pentoses) or other substituents present, (3) the stereochemical assignment of terminal monosaccharide units, (4) the sequence of the glycan part, (5) the interglycosidic linkages, and (6) the attachment points of the substituents to the aglycone (Abad-García et al., 2009).

HPLC coupled to mass spectrometry has been widely used to identify and quantify phenolic compounds. Electrospray ionization (ESI) mass spectrometric liquid interface provides advantages in terms of sensitivity and capability to analyze large, thermally labile, and highly polar compounds (Shui and Leong, 2004). Due to the diversity of unknown glycosidic flavonoids and/or bound phenolics found in fresh juices, polyphenolics may be quantified as aglycones, after hydrolysis. Moreover, the glycosylation of flavonoids was reported to decrease the antioxidant and α-glucosidase inhibitory activities (Sulaiman and Ooi, 2014). Qualitative and quantitative analysis of phenolics can be performed by ultrahigh performance liquid chromatography, UHPLC-MS/MS (Escudero-López et al., 2016). Different types of MS detectors may be used, such as ion trap (Borges et al., 2010; Mellisho et al., 2011; Gironés-Vilaplana et al., 2012a,b,2015), triple quadrupole (Escudero-López et al., 2016; Dag et al., 2017), and time-of-flight mass detectors (TOF) (Hoffmann et al., 2017). MS detectors are frequently preceded by PAD detectors scanning in the range 200–600 nm, and absorbance spectra and mass spectra are used to identify compounds reported previously in the literature. Samples may be analyzed in both positive and negative ionization modes, depending on the compounds. The positive ionization mode was used for anthocyanins determination while the negative ionization mode for other flavonoids (Gironés-Vilaplana et al., 2012a,b; Escudero-López et al., 2016).

Typical quantitative analysis of flavanones, hydroxycinnamic acids, and flavonols/flavones is accomplished by HPLC/PAD at 280, 330, and 350 nm, respectively (Mellisho et al., 2011).

12.2.2 Carotenoid Compounds

Carotenoids are a class of natural fat-soluble pigments that are found in numerous fruits and vegetables and more than 700 different carotenoids have been identified so far. They are 40-carbon highly unsaturated hydrocarbons derived from isoprene units and composed either entirely of carbon and hydrogen (carotenes, such as lycopene and β-carotene) or of carbon, hydrogen, and oxygen (xanthophylls, like zeaxanthin and lutein). Common carotenoids can have from 3 to 11 conjugated double bonds (in addition to unconjugated double bonds) and can undergo isomerization to yield mono- or poly-*cis* geometrical isomers. In the majority of foods, the all-*trans* configuration predominates (Kopec et al., 2012).

Carotenoids can be divided into provitamin A and non-provitamin A compounds, vitamin A being essential for the promotion of growth, embryonal development, and visual function. Moreover, they confer protection against different types of cancer, cardiovascular diseases, eye disorders (cataracts, macular degeneration), and skin damage through, mainly, their antioxidant, and anti-inflammatory properties (Vílchez et al., 2011).

12.2.2.1 Methodologies for the Determination of Carotenoid Compounds

The majority of carotenoids exhibit absorption in the visible region of the spectrum, in the range of 400–500 nm, which results from the long conjugated double-bond system of carotenoids. Most carotenoids maximally absorb at three wavelengths, resulting in three-peak spectra composed of band I (shorter wavelength), band II (middle absorption band), and band III (the longest wavelength band). Peak I may only occur as a "shoulder" in *cis*-carotenoids (Scott, 2001). The greater the number of conjugated double bonds, the higher the $\lambda_{\max}$ values and, at least seven conjugated double bonds are needed for a carotenoid to have appreciable color. Compared to the linear carotenoids, the spectra of cyclic forms develop a hypsochromic shift, hypochromic effect (decrease in absorbance), and loss of fine structure (spectrum with less-defined peaks). In addition, a carbonyl group in conjugation with the series of conjugated double bonds induces a bathochromic shift and loss of spectral fine structure, the three-maxima spectrum being replaced by a single broad curve. In comparison with *trans* forms, *cis*-isomerization of a chromophore's double bond causes a slight loss in color, small hypsochromic shift (usually 2–6 nm for mono-*cis*), and hypochromic effect, accompanied by the appearance of a cis peak in or near the UV region. The ratio of peak III/peak II can be useful to distinguish carotenoids and their isomers (Rodriguez-Amaya et al., 2001; Kopec et al., 2012).

C18 columns are often sufficient for separating different carotenoids (Table 12.2) (Sánchez-Moreno et al., 2006), although C30 columns allow better separation profile, especially of very similar compounds (Kopec et al., 2012).

12.2.3 Betalain Compounds

Betalains are water-soluble nitrogen-based plant pigments that replace the anthocyanins in flowers and fruits of plants from most families of the Caryophyllales, such as beetroot (*Beta vulgaris* L.) and dragon fruits (*Hylocereus* sp.). According to their chemical structure, they can range from red-violet (betacyanins) to yellow (betaxanthins) colors. Betacyanins are derivatives of betanidin, an iminium adduct of betalamic acid and cyclo-DOPA, while betaxanthins result from the condensation of amino acids or amines with betalamic acid (Gengatharan et al., 2015).

Among the health-promoting effects of betalains, antioxidant, anticancer, anti-lipidemic, and antimicrobial effects can be mentioned (Gengatharan et al., 2015).

12.2.3.1 Methodologies for the Determination of Betalain Compounds

Betacyanidins and betaxanthins can be monitored by HPLC-DAD using different wavelengths. Red-violet pigments show an absorption maxima at around 535 nm, while yellow betaxanthins absorb at 475 nm (Nollet and Toldra, 2012). Some authors also quantify the total betalain compounds spectrophotometrically at the same wavelengths (Wybraniec and Mizrahi, 2002; Ramli et al., 2014).

12.2.4 Vitamin C

Vitamin C (L-ascorbic acid and L-dehydroascorbic acid) is an essential water-soluble micronutrient in humans and is obtained through the diet, primarily from fruits and vegetables. Vitamin C was found to account for 65%–100% of the antioxidant potential of beverages derived from citrus fruit but <5% of apple and pineapple juice (Gardner et al., 2000).

12.2.4.1 Methodologies for the Determination of Vitamin C

Different types of HPLC columns, including C18 (Table 12.3) (Fontannaz et al., 2006; de Quirós et al., 2009; Mena et al., 2011; González-Molina et al., 2012), bonded-phase NH_2 (Rodríguez-Comesaña et al., 2002), polymeric columns (Lopes et al., 2006), and diol columns (Tai and Gohda, 2007) have been reported in the literature for the analysis of ascorbic acid in foodstuff. Regardless of the type of column, ascorbic acid detection was monitored by UV radiation at wavelengths that range from 243 to 261 nm (Table 12.3). Ascorbic acid and dehydroascorbic acid contents may be determined by reversed phase HPLC-UV (Table 12.3). The vitamin C content is calculated by the addition of ascorbic acid and dehydroascorbic acid contents (González-Molina et al., 2009). Ascorbic acid may be analyzed directly, without any sample pretreatment besides filtration (de Quirós et al., 2009). Total vitamin C determination by HPLC may be based on the reduction of dehydroascorbic acid to ascorbic acid, using DL-dithiothreitol as a reductant reagent (Sánchez-Moreno et al., 2003). Alternatively, the method of Ross may be used in which a solution of meta-phosphoric acid is added to samples (Gardner et al., 2000).

12.3 Pharmacological Activities of Fresh Juices and Flavored Waters

12.3.1 In Vitro Studies

The most widely used spectrophotometric/fluorescence methods to assess the antioxidant activity of juices and flavored

Table 12.3 Ascorbic Acid/Vitamin C Contents in Beverages Determined by HPLC

Beverage	Ascorbic acid (mg/L)	Total Vitamin C (mg/L)	Sample preparation	Chromatographic Analysis	References
Orange juice Apple juice Pineapple and grape juice Orange drink Lemon drink Apple drink Tea drink Isotonic drink Isotonic drink with orange flavor Isotonic drink with cola flavor	352 ± 6.0 739 ± 1.2 387 ± 1.3 840 ± 0.3 702 ± 0.6 201 ± 0.7 235 ± 0.2 30.2 ± 0.1 261 ± 0.8 263 ± 0.3 73.5 ± 0.7 175 ± 0.4 12.1 ± 0.03 17.8 ± 0.1 6.6 ± 0.01 183 ± 0.1 11.5 ± 0.2		Filtration and dilution when necessary	HPLC-UV Column: Tr-010065 Mediterranean Sea18 (15 × 0.4 cm, 3 μm) Mobile phase: Milli-Q water (0.1% v/v formic acid), 0.8 mL/min $V_{inj} = 20\ \mu L$ $\lambda_{det} = 245\ nm$	de Quirós et al. (2009)
Cantaloupe melon		120 ± 0.6	5 mL of juice were mixed with 1 mL 2.5% metaphosphoric acid. The mixture was centrifuged (4°C) at 1000 *g* for 10 min and filtered (0.45 μm)	HPLC-UV Column: C18 Luna (250 × 4.6 mm, 5 μm) Mobile phase: 25 mM KH_2PO_4 (pH 3.0); 1 mL/min $V_{inj} = 10\ \mu L$ $\lambda_{det} = 254\ nm$	Naknaen (2017)

Continued

Table 12.3 Table 12.3 Ascorbic Acid/Vitamin C Contents in Beverages Determined by HPLC—cont'd

Beverage	Ascorbic acid (mg/L)	Total Vitamin C (mg/L)	Sample preparation	Chromatographic Analysis	References
Pomegranate juices (26 samples)	n.d.—580			HPLC-PDA Column: Nucleosil C18 (250 × 4.6 mm, 5 μm) Mobile phase: containing 100 mg/L homocysteine and 200 mg/L EDTA, 0.6 mL/min at 40°C $\lambda_{det} = 265$ nm	Borges et al. (2010)
Pumpkin juice		80.0[a]	Juice samples were mixed with 10% metaphosphoric acid (1:1) and vortexed for 5 min and centrifuged (10,000 rpm, 5 min)	HPLC-UV Column: LiChrospher C18 (100 × 2.9 mm, 5 μm) Mobile phase: methanol (A) and 5 mM metaphosphoric acid pH 2.65 (B); gradient mode; 0.8 mL/min $\lambda_{det} = 245$ nm	Gliszczynska-Swiglo and Tyrakowska (2003), AlJahani and Cheikhousman (2017)
Tomato juice			40.0 mL of tomato juice + 25 mL of (3% metaphosphoric acid + 8% acetic acid). Centrifugation, filtration, adjust to 75 mL with distilled water. Filtration (0.45 μm)		Sánchez-Moreno et al. (2003), Sánchez-Moreno et al. (2006)
Freshly made	133 ± 1.3	165 ± 8.1			
Commercial pasteurized (6 samples)	76.5 ± 1.5–594 ± 7.1	919 ± 52–676 ± 45.5			

Commercial orange juice (7 samples)	249.81 ± 2.7–612.75 ± 13.9	308.80 ± 13.7–643.15 ± 27.8	Ascorbic acid: A volume of 50 mL of sample was homogenized with 40 mL of 30 g/L metaphosphoric acid + 80 g/L1% acetic acid). Filtration under suction and volume adjusted to 100 mL with water. Filtration (0.45 μm) Total vitamin C: An aliquot of the previous mixture was taken to react with 2 mL of 20 g/L dithiothreitol (2 h, in the dark). Filtration (0.45 μm)	HPLC-PAD Column: C-18 Hypersil ODS (250 × 4.6 mm, 5 μm) Mobile phase: 0.1 g/L H_2SO_4 solution pH 2.5–2.6, isocratic, 1.0 mL/min $V_{inj} = 20\ \mu L$ $\lambda_{det} = 245\ nm$	Sánchez-Moreno et al. (2003)
Fruit juices			Fresh juice samples were centrifuged at 2000 × *g* (4°C, 5 min) and 0.5 mL of supernatant were added to 0.5 mL 10% metaphosphoric acid. Vortex mixing (5 min), centrifugation (9000 × *g*, 4°C, 10 min)	HPLC-UV Column: Nucleosil ODS 55 mm (250 × 4.6 mm) Mobile phase: 25 mM myristyltrimethyl-ammonium bromide, 0.05 M NaOH, 0.06 M acetic acid, 7.5% (v/v) acetonitrile, pH 5.5. Homocysteine at 100 mg/mL and EDTA at 200 mg/mL were added; 1.0 mL/min $V_{inj} = 20\ \mu L$ $\lambda_{det} = 248\ nm$	Gardner et al. (2000)
Orange		1233 ± 36[b]			
Jaffa orange		1385 ± 36[b]			
Grapefruit		1076 ± 61[b]			
Pink grapefruit		920 ± 18[b]			
Florida orange		1008 ± 66[b]			
Apple		3.9 ± 0.5[b]			
Pineapple		4.4 ± 0.5[b]			
Vegetable		13 ± 5[b]			

[a] mg/100 g.

[b] μM.

waters are the 1,1-diphenyl-2-picrylhydrazyl (DPPH) scavenging activity, ferric reducing ability of plasma (FRAP), 2,2′-azino-bis-3-ethylbenzthiazoline-6-sulfonic acid (ABTS), oxygen radical absorbance capacity (ORAC), and metal chelating assays. Radicals are most commonly scavenged by two mechanisms, hydrogen atom transfer (HAT) or single electron transfer (SET). The DPPH assay is based on the reduction of the purple $DPPH^{\bullet}$ to the yellow 1,1-diphenyl-2-picryl hydrazine by antioxidants, a reaction that can be monitored at $\lambda = 517$ nm. Similarly, the ABTS assay is based on the generation of a blue/green $ABTS^{\bullet +}$ that can be reduced by antioxidants, and the more potent the antioxidant, the greater the decrease in absorbance at 734 nm. $ABTS^{\bullet +}$ can be generated by metmyoglobin-H_2O_2, potassium persulfate, or 2,2-azobis(2-amidinopropane) dihydrochloride (AAPH). The ORAC assay detects chemical change in a fluorescent molecule (fluorescein) caused by a free radical attack. When fluorescein is attacked by peroxyl radicals ($ROO^{\bullet}$), the fluorescence is lost. The role of the antioxidant is to slow the loss of fluorescence by quenching the peroxyl radicals. The FRAP assay is different from the previous three assays as there are no free radicals involved but the reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) is monitored. In this method, a rapid reduction in ferric-tripyridyltriazine (Fe^{3+}-TPTZ) by antioxidants present in the samples occurs, leading to the formation of ferrous-tripyridyltriazine (Fe^{2+}-TPTZ), a blue-colored product. The reaction is monitored at 620 nm (Floegel et al., 2011; Schaich et al., 2015).

The TAC and chemical composition of 39 water samples (29 flavored waters and 10 natural waters) as well as some of the flavors (tangerine, lime, strawberry, lemon, gooseberry, apple) used in their formulation were analyzed by Barroso et al. (2011d). With regard to the TFC, all flavors and flavored water samples had no flavonoids, in detectable amounts, in their composition. The richest samples in terms of TPC were the waters flavored with apple (284.0 mg GAE/L) or peach (147.0 mg GAE/L). Regarding the antioxidant activity, the samples that scored the best results were also the same (reducing power of apple water: 154.0 mg GAE/L; DPPH assay: apple—268.9 mg TEAC/L; peach—133.9 mg TEAC/L) and all flavored waters were more active than the natural ones. In addition, the flavor extracts of lime, lemon, and tangerine were analyzed by headspace-solid-phase microextraction-gas chromatography-mass spectrometry (HS-SPME/GC-MS) to obtain the qualitative and quantitative profiles of the volatile fraction of essential oils. A series of monoterpenes and sesquiterpenes were identified in all fractions, the main compounds being citral, α-limonene, carveol, and α-terpineol.

Sulaiman and Ooi (2014) compared the vitamin C content (by the titration method) and TPC, antioxidant activities, and α-glucosidase inhibitory activities of 40 fresh juices (Tables 12.4 and 12.5). The richest

Table 12.4 Antioxidant Activity of Fruit Juices Assessed by Spectrophotometric Methods

Common Name	DPPH Scavenging Activity	ABTS	FRAP	ORAC	Metal Chelating Assay	References
Banana	123.47 ± 0.91 µg VCEAC[a]/g sample	–	554.94 ± 4.55 µg TEAC[a]/g sample	–	40.22 ± 1.36%	Sulaiman and Ooi (2014)
Bilimbi	156.92 ± 0.58 µg VCEAC/g sample	–	192.66 ± 0.23 µg TEAC/g sample	–	81.33 ± 0.17%	Sulaiman and Ooi (2014)
Calamansi	185.83 ± 7.40 µg VCEAC/g sample	–	262.31 ± 1.40 µg TEAC/g sample	–	38.39 ± 0.75%	Sulaiman and Ooi (2014)
Carrot	69.91 ± 0.67 µg VCEAC/g sample	–	76.14 ± 0.30 µg TEAC/g sample	–	38.06 ± 3.78%	Sulaiman and Ooi (2014)
Cashew apple	4.07 mg TEAC/g	1.73 mg TEAC/g	1.34 mg VCEAC/g	–	–	Rodríguez et al. (2017)
Celery	78.00 ± 0.72 µg VCEAC/g sample	–	59.78 ± 0.11 µg TEAC/g sample	–	21.33 ± 0.50%	Sulaiman and Ooi (2014)
Ciruela	1.50 ± 0.24 µM TEAC/g fresh mass; 47.21 ± 5.95 mg VCEAC/100 g fresh mass	6.25 ± 0.04 µM TEAC/g fresh mass; 93.78 ± 0.60 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Coconut	102.79 ± 4.64 µg VCEAC/g sample	–	174.93 ± 0.82 µg TEAC/g sample	–	28.56 ± 1.92%	Sulaiman and Ooi (2014)
Dokong	111.27 ± 1.10 µg VCEAC/g sample	–	120.27 ± 0.41 µg TEAC/g sample	–	58.22 ± 5.51%	Sulaiman and Ooi (2014)
Gandaria	258.17 ± 4.25 µg VCEAC/g sample	–	133.31 ± 0.70 µg TEAC/g sample	–	23.00 ± 0.25%	Sulaiman and Ooi (2014)
Guava	517.95 ± 6.06 µg VCEAC/g sample	–	1924.34 ± 1.65 µg TEAC/g sample	–	44.06 ± 2.80%	Sulaiman and Ooi (2014)
Hippo apple	534.09 ± 1.41 µg VCEAC/g sample	–	2129.66 ± 2.04 µg TEAC/g sample	–	56.56 ± 0.77%	Sulaiman and Ooi (2014)

Continued

Table 12.4 Antioxidant Activity of Fruit Juices Assessed by Spectrophotometric Methods—cont’d

Common Name	DPPH Scavenging Activity	ABTS	FRAP	ORAC	Metal Chelating Assay	References
Indian gooseberry	613.71 ± 2.59 µg VCEAC/g sample	–	2784.89 ± 3.93 µg TEAC/g sample	–	18.67 ± 0.44%	Sulaiman and Ooi (2014)
Indian jujube	460.58 ± 17.93 µg VCEAC/g sample	–	484.79 ± 4.68 µg TEAC/g sample	–	22.11 ± 1.68%	Sulaiman and Ooi (2014)
Jackfruit	127.76 ± 1.35 µg VCEAC/g sample	–	142.94 ± 1.16 µg TEAC/g sample	–	–	Sulaiman and Ooi (2014)
Jackfruit	0.16 ± 0.03 µM TEAC/g fresh mass; 2.25 ± 0.42 mg VCEAC/100 g fresh mass	0.63 ± 0.01 µM TEAC/g fresh mass; 9.39 ± 0.18 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Jentik	233.21 ± 0.55 µg VCEAC/g sample	–	210.71 ± 3.24 µg TEAC/g sample	–	23.89 ± 4.89%	Sulaiman and Ooi (2014)
Lemon	3.7 mM TEAC	–	–	–	–	González-Molina et al. (2009)
	$\mathrm{IC}_{50} = 13.26 \pm 0.27$ mg/mL	–	–	–	–	Gironés-Vilaplana et al. (2012a)
Lemon + 5% acai	$\mathrm{IC}_{50} = 7.39 \pm 0.25$ mg/mL	–	–	–	–	Gironés-Vilaplana et al. (2012b)
Lemon + 5% black chokeberry	$\mathrm{IC}_{50} = 4.23$ mg/mL	–	–	–	–	Gironés-Vilaplana et al. (2012a)
Lemon + 5% blackthorn	$\mathrm{IC}_{50} = 9.55 \pm 0.83$ mg/mL	–	–	–	–	Gironés-Vilaplana et al. (2012b)
Lemon + 5% elderberry	~8.2 mM TEAC					González-Molina et al. (2012)
Lemon + 5% grape	~4.1 mM TEAC					González-Molina et al. (2012)
Lemon + 5% maqui	$\mathrm{IC}_{50} = 5.05 \pm 0.14$ mg/mL	–	–	–	–	Gironés-Vilaplana et al. (2012b)

Lemon + 5% noni	IC_{50} = 10.92 ± 1.20 mg/mL	–	–	–	–	Gironés-Vilaplana et al. (2015)
Lemon + 5% papaya	IC_{50} = 7.73 ± 0.39 mg/mL	–	–	–	–	Gironés-Vilaplana et al. (2015)
Lime	170.14 ± 5.32 μg VCEAC/g sample	–	347.61 ± 3.71 μg TEAC/g sample	–	11.56 ± 0.42%	Sulaiman and Ooi (2014)
Longan	61.37 ± 0.48 μg VCEAC/g sample	–	694.56 ± 4.76 μg TEAC/g sample	–	–	Sulaiman and Ooi (2014)
Malabar tamarind	115.14 ± 1.15 μg VCEAC/g sample	–	168.27 ± 0.74 μg TEAC/g sample	–	36.22 ± 1.67%	Sulaiman and Ooi (2014)
Malay apple	137.11 ± 2.07 μg VCEAC/g sample	–	189.94 ± 2.95 μg TEAC/g sample	–	22.67 ± 0.29%	Sulaiman and Ooi (2014)
Mangaba	5.27 ± 0.34 μM TEAC/g fresh mass; 118.78 ± 9.43 mg VCEAC/100 g fresh mass	10.84 ± 0.13 μM TEAC/g fresh mass; 162.57 ± 2.02 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Mango	133.75 ± 9.61 μg VCEAC/g sample	–	311.13 ± 2.66 μg TEAC/g sample	–	25.33 ± 1.33%	Sulaiman and Ooi (2014)
Mangosteen	225.70 ± 9.23 μg VCEAC/g sample	–	171.48 ± 0.79 μg TEAC/g sample	–	71.83 ± 1.17%	Sulaiman and Ooi (2014)
Melon	98.13 ± 1.18 μg VCEAC/g sample	–	123.44 ± 1.11 μg TEAC/g sample	–	–	Sulaiman and Ooi (2014)
Murici	6.46 ± 0.31 μM TEAC/g fresh mass; 295.12 ± 26.87 mg VCEAC/100 g fresh mass	15.73 ± 0.01 μM TEAC/g fresh mass; 235.94 ± 0.12 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Nam nam	105.28 ± 0.41 μg VCEAC/g sample	–	60.86 ± 1.18 μg TEAC/g sample	–	63.61 ± 1.11%	Sulaiman and Ooi (2014)
Nutmeg	242.54 ± 1.08 μg VCEAC/g sample	–	229.74 ± 0.85 μg TEAC/g sample	–	28.61 ± 2.43%	Sulaiman and Ooi (2014)
Orange	58.1 ± 2.6%	5.4 ± 0.1 mmol TEAC/L	10.3 ± 0.4 mmol Fe^{2+}/L	6044 ± 247 μmol TEAC/L	–	Escudero-López et al. (2013)

Continued

Table 12.4 Antioxidant Activity of Fruit Juices Assessed by Spectrophotometric Methods—cont'd

Common Name	DPPH Scavenging Activity	ABTS	FRAP	ORAC	Metal Chelating Assay	References
Papaya	202.78 ± 0.61 μg VCEAC/g sample	–	469.44 ± 1.05 μg TEAC/g sample	–	7.89 ± 5.97%	Sulaiman and Ooi (2014)
	2.24 ± 0.06 μM TEAC/g fresh mass; 54.00 ± 0.20 mg VCEAC/100 g fresh mass	7.60 ± 0.20 μM TEAC/g fresh mass; 114.04 ± 2.96 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Pineapple	105.55 ± 1.42 μg VCEAC/g sample	–	172.45 ± 1.99 μg TEAC/g sample	–	9.11 ± 4.52%	Sulaiman and Ooi (2014)
	1.33 ± 0.06 μM TEAC/g fresh mass; 16.59 ± 0.86 mg VCEAC/100 g fresh mass	3.78 ± 0.03 μM TEAC/g fresh mass; 58.59 ± 3.00 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Pomegranate	15.5 mM TEAC	–	–	–	–	González-Molina et al. (2009)
		21.96 ± 1.53 mM TEAC	–	–	–	Hong et al. (2016)
Pommelo	397.68 ± 4.21 μg VCEAC/g sample	–	834.22 ± 7.28 μg TEAC/g sample	–	–	Sulaiman and Ooi (2014)
Pulasan	49.19 ± 0.68 μg VCEAC/g sample	–	73.06 ± 0.29 μg TEAC/g sample	–	72.78 ± 1.13%	Sulaiman and Ooi (2014)
Rambai	96.88 ± 0.34 μg VCEAC/g sample	–	116.64 ± 0.67 μg TEAC/g sample	–	10.78 ± 1.11%	Sulaiman and Ooi (2014)
Rambutan	94.17 ± 1.60 μg VCEAC/g sample	–	96.85 ± 1.37 μg TEAC/g sample	–	3.39 ± 1.92%	Sulaiman and Ooi (2014)
Santol, kechapi	418.22 ± 5.17 μg VCEAC/g sample (mature flesh)	–	933.39 ± 2.21 μg TEAC/g sample	–	24.67 ± 0.44%	Sulaiman and Ooi (2014)
	116.20 ± 0.46 μg VCEAC/g sample (ripe aril)	–	97.01 ± 0.70 μg TEAC/g sample	–	Pure juice: 56.72 ± 1.18%	Sulaiman and Ooi (2014)

Sapodilla	116.55 ± 0.74 µg VCEAC/g sample	–	759.90 ± 17.34 µg TEAC/g sample	–	–	Sulaiman and Ooi (2014)
	0.17 ± 0.01 µM TEAC/g fresh mass; 3.51 ± 0.55 mg VCEAC/100 g fresh mass	0.99 ± 0.11 µM TEAC/g fresh mass; 14.82 ± 1.57 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Snake fruit	421.56 ± 8.61 µg VCEAC/g sample	–	1556.79 ± 8.73 µg TEAC/g sample	–	–	Sulaiman and Ooi (2014)
Soursop	132.57 ± 1.67 µg VCEAC/g sample	–	210.80 ± 3.18 µg TEAC/g sample	–	–	Sulaiman and Ooi (2014)
	1.36 ± 0.01 µM TEAC/g fresh mass; 16.94 ± 0.06 mg VCEAC/100 g fresh mass	6.09 ± 0.13 µM TEAC/g fresh mass; 91.29 ± 2.06 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Star fruit	111.88 ± 1.36 µg VCEAC/g sample	–	154.55 ± 3.32 µg TEAC/g sample	–	78.94 ± 0.42%	Sulaiman and Ooi (2014)
Sugar cane	124.37 ± 1.97 µg VCEAC/g sample	–	159.01 ± 0.65 µg TEAC/g sample	–	71.00 ± 0.17%	Sulaiman and Ooi (2014)
Sweetsop, sugar-apple	145.57 ± 1.50 µg VCEAC/g sample	–	146.92 ± 0.09 µg TEAC/g sample	–	24.56 ± 0.35%	Sulaiman and Ooi (2014)
	0.68 ± 0.01 µM TEAC/g fresh mass; 8.56 ± 0.12 mg VCEAC/100 g fresh mass	6.21 ± 0.62 µM TEAC/g fresh mass; 93.16 ± 9.38 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Tamarind	2.04 ± 0.48 µM TEAC/g fresh mass; 47.25 ± 10.28 mg VCEAC/100 g fresh mass	8.32 ± 0.11 µM TEAC/g fresh mass; 124.70 ± 1.58 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)
Umbu	0.70 ± 0.16 µM TEAC/g fresh mass; 8.85 ± 2.06 mg VCEAC/100 g fresh mass	1.07 ± 0.00 µM TEAC/g fresh mass; 18.49 ± 3.53 mg VCEAC/100 g fresh mass	–	–	–	Almeida et al. (2011)

Continued

Table 12.4 Antioxidant Activity of Fruit Juices Assessed by Spectrophotometric Methods—cont'd

Common Name	DPPH Scavenging Activity	ABTS	FRAP	ORAC	Metal Chelating Assay	References
Watermelon	74.64 ± 0.70 μg VCEAC/g sample	–	37.81 ± 0.39 μg TEAC/g sample	–	32.89 ± 4.62%	Sulaiman and Ooi (2014)
Wax apple	149.77 ± 2.61 μg VCEAC/g sample	–	625.18 ± 0.84 μg TEAC/g sample	–	82.28 ± 0.10%	Sulaiman and Ooi (2014)
Wild mango	289.00 ± 3.25 μg VCEAC/g sample	–	866.82 ± 10.69 μg TEAC/g sample	–	24.83 ± 0.17%	Sulaiman and Ooi (2014)

[a] *TEAC*, trolox equivalent antioxidant activity; *VCEAC*, vitamin C equivalent antioxidant activity.

Table 12.5 Enzyme Inhibition Activities of Fruit Juices Assessed by Spectrophotometric Methods

Common Name	α-Glucosidase Inhibition[a]	Acetylcholinesterase Inhibition[b]	Butyrylcholinesterase Inhibition[c]	References
Calamansi	75.24 ± 0.17%	–	–	Sulaiman and Ooi (2014)
Gandaria	83.44 ± 0.10%	–	–	Sulaiman and Ooi (2014)
Hippo apple	93.75 ± 0.14%	–	–	Sulaiman and Ooi (2014)
Indian gooseberry	95.37 ± 0.15%	–	–	Sulaiman and Ooi (2014)
Lemon	–	IC_{50} = 13.18 ± 0.08 mg/mL	IC_{50} = 12.82 ± 0.21 mg/mL	Gironés-Vilaplana et al. (2012a)
Lemon + 5% acai	–	IC_{50} = 8.83 ± 0.11 mg/mL	IC_{50} = 8.61 ± 0.14 mg/mL	Gironés-Vilaplana et al. (2012b)
Lemon + 5% blackthorn	–	IC_{50} = 10.44 mg/mL	IC_{50} = 10.40 ± 0.26 mg/mL	Gironés-Vilaplana et al. (2012b)
Lemon + 5% black chokeberry	–	IC_{50} = 10.57 mg/mL	IC_{50} = 10.89 mg/mL	Gironés-Vilaplana et al. (2012a)
Lemon + 5% maqui	–	IC_{50} = 13.70 ± 0.70 mg/mL	IC_{50} = 13.38 ± 0.19 mg/mL	Gironés-Vilaplana et al. (2012b)
Lemon + 5% noni	–	IC_{50} = 9.07 ± 0.64 mg/mL	IC_{50} = 11.92 ± 0.72 mg/mL	Gironés-Vilaplana et al. (2015)
Lemon + 5% papaya	–	IC_{50} = 7.64 ± 0.14 mg/mL	IC_{50} = 7.54 ± 0.16 mg/mL	Gironés-Vilaplana et al. (2015)
Malabar tamarind	65.94 ± 0.32%	–	–	Sulaiman and Ooi (2014)
Mangosteen	85.20 ± 0.59%	–	–	Sulaiman and Ooi (2014)
Nam nam	88.59 ± 0.34%	–	–	Sulaiman and Ooi (2014)
Nutmeg	86.98 ± 0.23%	–	–	Sulaiman and Ooi (2014)
Santol, kechapi	46.15 ± 5.22%	–	–	Sulaiman and Ooi (2014)
Wax apple	79.44 ± 0.45%	–	–	Sulaiman and Ooi (2014)
Wild mango	64.85 ± 3.24%	–	–	Sulaiman and Ooi (2014)

[a] The assay for α-glucosidase inhibition is based on the conversion of the substrate 4-nitrophenyl-α-D-glucopyranoside to α-D-glucopyranoside and 4-nitrophenol, the *yellow color* of the latter being measured at 405 nm.

[b] Based on Ellman's method: colorimetric method based on the measurement of thiocholine released during the process of acetylthiocholine/*S*-butyrylthiocholine chloride hydrolysis under the influence of AChE/BuChE. The number of free thiocholine molecules is quantified spectrophotometrically by the reaction with 5,5-dithiobis-(2-nitrobenzoic acid) (DTNB), whose product of the reaction (5-thio-2-nitrobenzoate anion), presents a *yellow color* at $\lambda = 405$ nm.

juices in terms of TPC and vitamin C contents were those of guava (857.2 μg GAE/g sample and 590.3 μg AAE/g sample) and hippo apple (790.4 μg GAE/g sample and 108.2 μg AAE/g sample). Concerning the bioactivities, Indian gooseberry juice exhibited the strongest scavenging activity against DPPH (613.7 μg VCEAC/g sample), reducing power (2784.9 μg TEAC/g sample), and α-glucosidase inhibitory activities (95.4%), followed by that of hippo apple. Therefore, the authors decided to explore the chromatographic profile of both juices using ultra-performance liquid chromatography (UPLC) coupled with PAD analysis. Concerning hippo apple juice, ellagic acid, one myricetin derivative, and one quercetin derivative were detected, which, after hydrolysis, corresponded to 1269.5 mg/100 g extract of ellagic acid, 265.6 mg/100 g extract of myricetin, and 61.7 mg/100 g extract of quercetin (Table 12.2). Indian gooseberry juice contained gallic acid, two quercetin derivatives, a myricetin derivative, dihydroquercetin (= taxifolin), and kaempferol, resulting in 230.7, 103.3, 85.4, 142.7, and 4.5 mg/100 g of extract of gallic acid, dihydroquercetin, myricetin, quercetin, and kaempferol, respectively, after hydrolysis (Table 12.2).

Gironés-Vilaplana et al. (2012a,b, 2015) and González-Molina et al. (2012) prepared blends of lemon juice with 5% (*w*/*v*) of other fruits (black chokeberry, maqui, noni, acai, papaya, grape, elderberry, and blackthorn) and analyzed them by HPLC-DAD-ESI/MS^n (Fig. 12.1). The amount of phenolic compounds in each blend ranged from 15.1 mg/100 mL (lemon juice + 5% papaya) to 117.2 mg/100 mL (lemon juice + 5% black chokeberry). Lemon juice contributed to the blends with flavonols (quercetin derivatives), flavanones (eriodictyol and hesperetin derivatives), flavones (apigenin and diosmetin derivatives) (Gironés-Vilaplana et al., 2012a,b; González-Molina et al., 2012; Gironés-Vilaplana et al., 2015), hydroxycinnamic acids (3-*O*- and 5-*O*-caffeoylquinic, ferulic, and sinapic acids) (Gironés-Vilaplana et al., 2012a,b), and vitamin C (ascorbic acid + dehydroascorbic acid) (González-Molina et al., 2012). In addition, chokeberry contributed with anthocyanins (cyanidin derivatives), flavonols (quercetin derivatives), and 3-*O*-caffeoylquinic acid (Gironés-Vilaplana et al., 2012a) (Table 12.2); maqui with anthocyanins (delphinidin and cyanidin derivatives), ellagic acid derivatives, flavonols (myricetin and quercetin derivatives), and 5-*O*-caffeoylquinic acid (Gironés-Vilaplana et al., 2012b); acai was characterized by the presence of anthocyanins (cyanidin and malvidin derivatives), quercetin glycosides, 3-*O*- and 5-*O*-caffeoylquinic acids, and 5-*O*-*p*-coumaroylquinic acid (Gironés-Vilaplana et al., 2012b); blackthorn contained cyanidin, peonidin, and quercetin derivatives as well as several hydroxycinnamic acids (Gironés-Vilaplana et al., 2012b); papaya contributed with quercetin derivatives and xanthones (mangiferin, mangiferin gallate, and isomangiferin gallate) (Gironés-Vilaplana et al., 2015); noni was characterized by the presence of flavonol glycosides

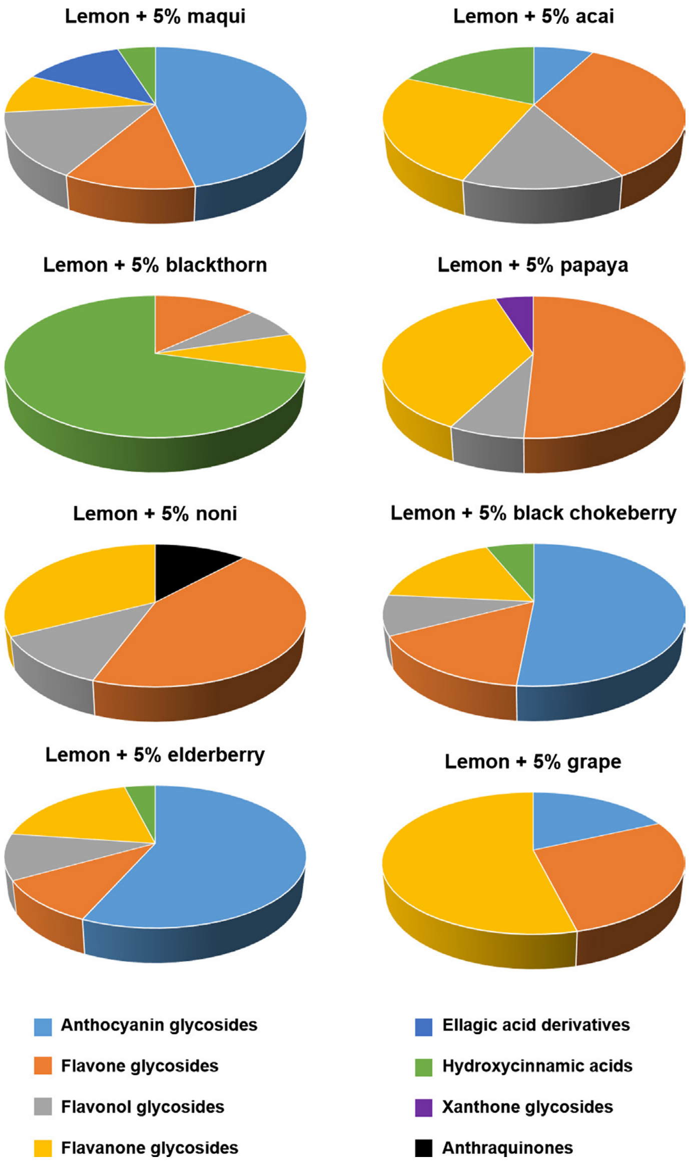


Fig. 12.1 Comparison between different classes of phenolic compounds present in lemon juice blended with maqui, acai, blackthorn, papaya, noni, black chokeberry, elderberry, and grape.

(quercetin and kaempferol derivatives) and one anthraquinone (lucidin) (Gironés-Vilaplana et al., 2015); grape contributed with several 3-*O*-glucosides of delphinidin, petunidin, peonidin, and malvidin (González-Molina et al., 2012); and elderberry with cyanidin glycosides, quercetin-3-*O*-glucoside, and 5-*O*-caffeoylquinic acid (González-Molina et al., 2012). The scavenging activity as well as the ability of these blends to inhibit enzymes related to Alzheimer's disease were assessed. Pure lemon juice displayed the following activities: $IC_{50} = 13.3$ mg/mL (against DPPH), 5.2 mg/mL (against superoxide anion radical), 25.6 mg/mL (against hypochlorous acid), and 6.9 mg/mL (against hydroxyl radical). The DPPH scavenging activity (Table 12.4) of the blends varied from $IC_{50} = 4.3$ mg/mL (lemon + 5% black chokeberry) to $IC_{50} = 10.9$ mg/mL (lemon + 5% noni), superoxide anion radical scavenging from $IC_{50} = 2.2$ mg/mL (lemon + 5% noni) to $IC_{50} = 4.4$ mg/mL (lemon + 5% acai), hypochlorous acid scavenging activity from $IC_{50} = 15.3$ mg/mL (lemon + 5% maqui) to $IC_{50} = 29.0$ mg/mL (lemon + 5% black chokeberry), and hydroxyl radical scavenging activity from $IC_{50} = 2.8$ mg/mL (lemon + 5% maqui) to $IC_{50} = 3.9$ mg/mL (lemon + 5% noni). Lemon + 5% papaya blend was the most potent acetylcholinesterase (AChE; $IC_{50} = 7.6$ mg/mL) and butyrylcholinesterase (BuChE; $IC_{50} = 7.5$ mg/mL) inhibitor (Table 12.5).

Pomegranates are characterized by the presence of ellagitannins and anthocyanins (Borges et al., 2010). Lemon fruit (*Citrus limon* (L.) Burm. f.) is a rich source of nutrients, including flavonoids, citric acid, vitamin C, and minerals (e.g., potassium), which provide numerous health-promoting properties (González-Molina et al., 2009). Lemon juice is widely used as an antioxidant natural substitute for the synthetic ascorbic or citric acids, E300 and E330, respectively (González-Molina et al., 2009).

Lemon and pomegranate juices were also combined in different proportions (75% + 25%, 50% + 50%, and 25% + 75% of lemon + pomegranate juices, respectively) (González-Molina et al., 2009). The most promising one, from the chemical and biological points of view, was that composed of 75% pomegranate + 25% lemon as it contained high amounts of phenolic compounds (≈200 mg GAE/100 mL) combined with ascorbic acid and high antioxidant activity (≈12 mM Trolox against DPPH radical). HPLC-DAD analysis of pomegranate juice revealed the presence of hydrolysable tannins (punicalagins 1 and 2), ellagic acid, and several delphinidin, cyanidin, and pelargonidin glycosides, which contributed to the antioxidant activity observed. The authors noticed that, during storage (70 days), lemon juice reduced punicalagin hydrolysis as this reaction is favored at $pH \approx 7$ and negatively affected anthocyanin stability, as the combination of both classes of compounds resulted in their degradation through a condensation reaction.

Borges et al. (2010) determined the phenolic profile using HPLC-DAD-MS^2 and vitamin C content using HPLC-DAD of 36 commercial juices (6 100% pomegranate juices, 20 diluted pomegranate juice or pomegranate blended with other fruit juices, and 10 non-pomegranate fruit juices) as well as their antioxidant activity through ABTS, FRAP, and ORAC assays. Seventeen anthocyanins (delphinidin, cyanidin, and pelargonidin glycosides), ellagitannins (punicalagin-like, punicalagin isomer, punicalins A and B, 2-*O*-galloylpunicalagin, punicalagins A and B, and granatins A and B) and ellagic acid derivatives (ellagic acid-*O*-hexoside and ellagic acid) were identified in the 26 pomegranate and pomegranate blend juices. The richest samples were the pure pomegranate juices (635–2043 μM of phenolic compounds) as well as that composed of pomegranate (25%) and blueberry (5%) (1115 μM). The highest vitamin C contents were obtained for juices containing in their composition 29% of pomegranate and 7% of aronia (38.0 mg/100 mL), 14% pomegranate, 10.5% cranberry, 6.5% apple and vitamin C (48.2 mg/100 mL), 9% pomegranate, 3% raspberries, 1.7% black currant, 1% cranberry, 0.7% strawberry and apple, white grapes and vitamins C and E (38.5 mg/100 mL), and 8% pomegranate/raspberry and vitamin C (58.0 mg/100 mL). 100% pomegranate juices contained the highest total phenolic content (10.3–20.7 mmol GAE/L) and antioxidant activity (FRAP—24.1–55.3 mmol Fe^{2+} eq./L; ORAC—34.5–85.8 mmol TEAC/L; ABTS—17.9–41.3 mmol TEAC/L). Two other samples also scoring strong antioxidant activity included juices that have in their composition pomegranate (25%) and blueberry (5%) and pomegranate (32%), and aronia (5%). Additional analysis was conducted on seven juices using HPLC-ABTS on-line antioxidant activity. For 100% pomegranate juices, the major contributors to the antioxidant activity were the ellagitannins, while in the juice composed of 29% of pomegranate and 7% of aronia and in that composed of 8% pomegranate/raspberry and vitamin C, vitamin C was the main compound responsible for the antioxidant activity.

Raúl et al. (2016) prepared binary and ternary mixtures of orange (var. Washington navel), grape (var. Alfonso Lavallet), and starfruit juices (var. Golden Star) and the antioxidant capacity of each sample was determined by DPPH radical scavenging capacity. They observed that the antioxidant capacity was higher in mixtures than in pure juices, indicating that binary mixtures of orange and starfruit juices ($IC_{50} = 31.3\ \mu L$) and ternary mixtures ($IC_{50} = 31.4$–$36.3\ \mu L$) were the most potent ones. Higher antioxidant capacity of orange and starfruit binary mixtures could be due to the high concentration of ascorbic acid in the first species (67 mg of ascorbic acid/100 g) and phenolic compounds in the second one (131 mg of total phenols/100 g), while the antioxidant properties of a ternary mixture (1/6 orange juice, 4/6 grape juice, and 1/6 starfruit juice) could also be due to the high presence of anthocyanins, quercetin, quercetin-3-*O*-rutinoside, catechin, and resveratrol, in grape juice.

Antolak et al. (2017) evaluated the antioxidant activity of three different juices (elderberry, lingonberry, and cornelian cherry) as well as their effect against adhesion of bacterial strains of *Asaia lannensis* and *Asaia bogorensis*. Regarding chemical composition, sugar content was determined enzymatically using a UV spectrophotometer and

TPC was calculated by the Folin-Ciocalteu method. Fructose concentration was between 3.3 (elderberry) and 5.6 mg/100 mL (cornelian cherry); glucose between 3.0 (cornelian cherry) and 4.5 mg/100 mL (lingonberry); and TPC ranged from 2.3 (cornelian cherry) to 8.0 mg GAE/mL (elderberry). Moreover, LC-MS analyses of the phenolic profile were carried out. Cornelian cherry juice was characterized by the presence of anthocyanins (cyanidin and pelargonidin glycosides), hydroxybenzoic acids (gallic and protocatechuic acids), and hydroxycinnamic acids (cinnamic, *p*-coumaric and rosmarinic acids) (Table 12.2). Lingonberry juice contained the same phenolic acids besides 4-hydroxybenzoic acid, flavan-3-ols (catechin and epicatechin), and anthocyanins (cyanidin and petunidin glucosides). In elderberry juice, the authors identified several phenolic acids (caffeic gallic, protocatechuic, rosmarinic, 4-hydroxybenzoic acids), quercetin-3-*O*-rutinoside, delphinidin-3-*O*-glucoside, and three glycosides of cyanidin (Table 12.2). In terms of antioxidant activity, cornelian cherry juice showed the strongest DPPH scavenging activity ($IC_{50} = 0.045$ g/mL), while the lowest capacity was obtained for elderberry juice ($IC_{50} = 0.072$ g/mL). The FRAP test results indicated that the elderberry juice ($IC_{50} = 0.021$ g/mL) displayed the strongest activity, followed by lingonberry juice ($IC_{50} = 0.030$ g/mL). These results pointed out a correlation between the antioxidant activity and the total phenolic content. Finally, phenolic compounds were also responsible for the reduction of *Asaia* spp. adhesion to glass, polystyrene, and PET.

12.3.2 Total Antioxidant Capacity Evaluation Using a DNA-Based Sensor

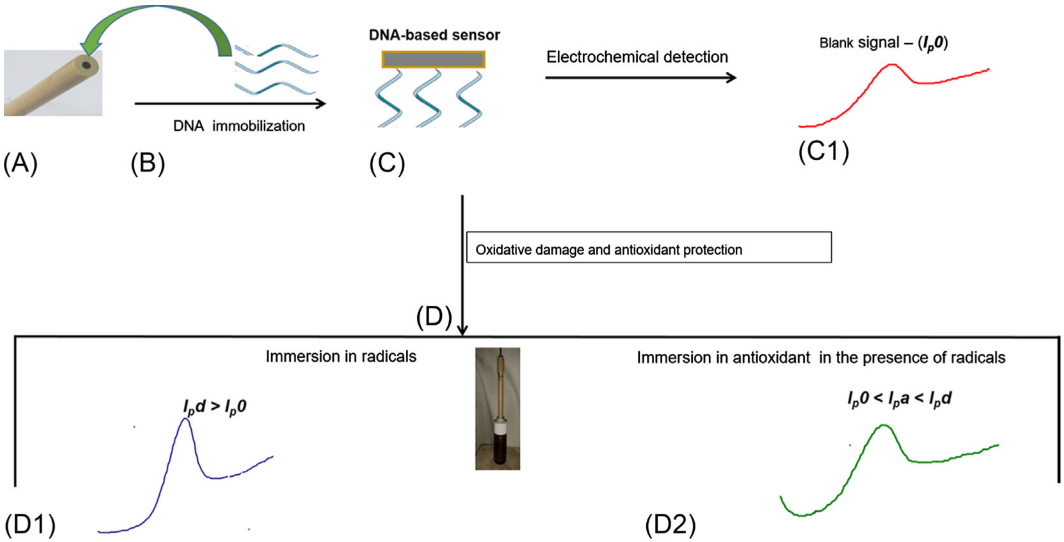
The use of electrochemical methods for the TAC evaluation presents several advantages over other methods, because these techniques have a short detection time, only need small volume of samples, are simple to use, and most importantly, there is a minimization of the interferences from colored samples avoiding time-consuming pretreatments (Barroso et al., 2016).

Generically, electrochemical methods are related to the physical chemistry field that studies the relationship between electricity, as a measurable and quantitative analytical parameter (e.g., current intensity, potential), and identifiable chemical change. These reactions involve electric charges moving between electrodes and an electrolyte. The achievement of electrochemical measurements is influenced by the electrode material (usually called working electrode), which can be made on carbon, gold, platinum, and silver among several others (Barroso et al., 2014).

Considering that antioxidants usually exhibit native electroactivity, this property can be used for quantitative purposes namely for antioxidant analysis (Cruz et al., 2015). For antioxidant detection, the most common electrochemical techniques used are cyclic- (CV), square wave- (SWV), and differential pulse voltammetry (DPV).

The use of electrochemical DNA-based biosensors for antioxidant determination is a reasonable option because the protective role of antioxidants at the cellular level could be properly studied by assessing DNA integrity (Barroso et al., 2011a; Cruz et al., 2015). In this way, an in vivo assay (mimicking the biological processes that occur in the biological cell) can be simulated by exposing DNA layers to biological free radicals and antioxidants (similarly to what occurs in the cell nucleus) (Barroso et al., 2011a).

The construction of DNA-based sensors is mostly based on the DNA-based material immobilization by physical adsorption onto carbon paste electrodes (CPEs) (Scheme 12.1). Then, this biosensor is exposed to: (a) Oxidative damage by immersing the DNA-based CPE in radical solutions (hydroxyl ($HO^{\bullet}$), superoxide ($O_2^{\bullet-}$), sulfate ($SO_4^{\bullet-}$), or nitric oxide ($^{\bullet}NO$) radical). Electrochemically, this oxidative lesion can be observed by the decrease of the peak current (ip) of the DNA



Scheme 12.1 DNA-based sensor design: (A) CPE transducer; (B) DNA immobilization onto CPE surface; (C) DNA-based sensor; (C1) electrochemical blank signal; (D) immersion of the DNA-based sensor in (D1) radicals and (D2) in antioxidant in the presence of radicals. Adapted from Cruz, D., Barroso, M.F., Alves, R.C., González-García, M.B., Ramalhosa, M.J., Duarte, A.J., Oliveira, M.B.P.P., Delerue-Matos, C., 2015. Assay of total antioxidant capacity of coffee: use of a DNA-based biosensor. In: Preedy, V. R. (Ed.), Coffee: In Health and Disease Prevention. Academic Press, Elsevier, 963–970; Barroso, M.F., Ramalhosa, M.J., Alves, R.C., Dias, A., Soares, C.M.D., Oliva-Teles, M.T., Delerue-Matos, C., 2016. Total antioxidant capacity of plant infusions: assessment using electrochemical DNA-based biosensor and spectrophotometric methods. Food Control 68 (Suppl. C), 153–161.

material; (b) Protective effect promoted by antioxidants, in the presence of radicals, on the DNA layers. In this process, an increase of the ip is observed.

Some reports indicate the use of DNA-based sensors for the total antioxidant activity assessment in beverages such as flavored waters and juices (Barroso et al., 2011b,c, 2012; Cruz et al., 2016). Table 12.6 shows the TAC (expressed in mg AAE L^{-1}) values obtained for commercial drinks (flavored waters and fruit juices) using $O_2^{\bullet -}$, $HO^{\bullet}$, $SO_4^{\bullet -}$, and $^{\bullet}NO$ radicals to promote DNA damage (Barroso et al., 2011b,c, 2012,; Yang et al., 2013; Cruz et al., 2016).

As it is possible to observe (Table 12.6), fruit juice presented higher TAC values than flavored waters. This behavior was expected as fruit juice was already reported as a significant source of dietary antioxidants (Cruz et al., 2015).

12.3.3 In Vivo Studies

The complete set of low-molecular-weight metabolites in a biological sample is called the metabolome. It can be divided into three main fractions: the endogenous metabolome that includes all metabolites produced by a cell, a tissue, or an organism; the microbial metabolome produced by the microbiota; and the xenometabolome that includes all exogenous metabolites derived from drugs, pollutants, and food products. The concentration of metabolites resulting from phytochemicals digestion generally increases in plasma and urine proportionally to the amount ingested. Thus, endogenous metabolites and exogenous phytochemical metabolites produce a signature characteristic of the intake of a given phytochemical and this signature gathers detailed information about the phytochemical intake and the effects these phytochemicals have on the human metabolism (Manach et al., 2009). Thus, understanding the role of these biomarkers in human health will allow us to give better nutritional advice to the consumers.

In a human trial, eight volunteers consumed 400 mL of citrus juice (a mixture of orange and lemon juices) daily for 4 consecutive days and urine samples were collected before intake and 24 h after each citrus juice intake. The urine samples were analyzed by nano-HPLC-q-TOF, allowing the identification of four endocrine compounds (tetrahydroaldosterone-3-glucuronide, cortolone-3-glucuronide, testosterone-glucuronide, and 17-hydroxyprogesterone) belonging to the steroid biosynthesis pathway, as significant metabolites upregulated by citrus juice intake (Medina et al., 2013).

Llorach et al. (2014) used an HPLC-q-TOF metabolomic approach in order to analyze the changes in the human urine metabolome of 51 human subjects (23 men and 28 women) following regular intake

Table 12.6 Antioxidant Activity Obtained for Commercial Drinks Measured by a DNA-Based Sensor

Drinks	Free Rradical Used	TAC (mg AAE L^{-1})
Flavored waters		
Lemon	$O_2^{\bullet -}$	0.5–19
Pineapple		1.0–1.7
Apple		0.3–3.7
Orange		0.8–7.3
Lemon	$HO^{\bullet}$	3.3–36
Pineapple		14–38
Apple		4.4–5.0
Orange		3.0–4.6
Lemon	$SO_4^{\bullet -}$	2.6–11.9
Pineapple		5.9–10.9
Apple		3.8–13.8
Orange		2.4–6.4
Orange	$^{\bullet}NO$	73.9
Fruit juices		
Orange	$HO^{\bullet}$	231.5
Grape		182.6
Pear		113.2
Orange	$^{\bullet}NO$	167.2–483.4

Adapted from Barroso, M.F., de-los-Santos-Álvarez, N., Delerue-Matos, C., Oliveira, M.B.P.P., 2011. Towards a reliable technology for antioxidant capacity and oxidative damage evaluation: electrochemical (bio)sensors. Biosens. Bioelectron. 30 (1), 1–12; Barroso, M.F., Delerue-Matos, C., Oliveira, M.B.P.P., 2011. Electrochemical DNA-sensor for evaluation of total antioxidant capacity of flavours and flavoured waters using superoxide radical damage. Biosens. Bioelectron. 26 (9), 3748–3754; Barroso, M.F., Delerue-Matos, C., Oliveira, M.B.P.P., 2012. Electrochemical evaluation of total antioxidant capacity of beverages using a purine-biosensor. Food Chem. 132 (2), 1055–1062; Yang, Y., Zhou, J., Zhang, H., Gai, P., Zhang, X., Chen, J., 2013. Electrochemical evaluation of total antioxidant capacities in fruit juice based on the guanine/graphene nanoribbon/glassy carbon electrode. Talanta 106 (Suppl. C), 206–211.

of aronia (5%)-citrus (95%) juice (250 mL/day) for 16 weeks. The results showed that biomarkers of aronia-citrus juice intake found in urine included the metabolites proline, betaine, ferulic acid, and two unknown mercapturate derivatives. In a parallel study, control and triathlete volunteers ($n=8$ and $n=15$, respectively) were given 400 and 200 mL of 5% aronia-95% citrus juice, respectively. Twenty-four hour urine samples of both groups of volunteers were characterized by the presence of glucuronides, sulfates, and sulfo-glucuronides of naringenin, hesperetin, isosakuranetin, eriodictyol, and homoeriodictyol as well as the corresponding aglycones. Samples were then hydrolyzed by urine β-glucuronidase to determine the flavanones concentration by UPLC-QqQ-MS/MS, and the total excretion of flavanones increased five times in the triathletes compared with the control volunteers (1860 vs 376 nmol/24 h, respectively). The aglycones naringenin, eriodictyol, and hesperetin were the flavanones that contributed more significantly to the increase of the total urinary flavanones. Moreover, the ninefold increase of homoeriodictyol in triathletes' urine compared to that of control volunteers may suggest an overactivation of the microbiota metabolism caused by physical exercise (Medina et al., 2012). In a second part of the clinical trial, the triathletes underwent elite training for 2 weeks and eriodictyol and hesperetin excretion increased thanks to the additional flavanones intake provided by the juice (Medina et al., 2012). In further exploration of the effects of this juice blend, clinical trials composed of 16 elite triathletes were constituted to assess the role of juice and chronic exercise against DNA damage (Garcia-Flores et al., 2016a) and against oxidative damage in the central nervous system (CNS) (Garcia-Flores et al., 2016b), since during chronic training, an increase in oxidative/nitrosative stress products was detected. Under oxidative and nitrosative stresses, the DNA bases are prone to oxidation or nitration. The intake of 5% aronia-95% citrus juice during the training period resulted in the maintenance of the plasmatic cGMP levels, suggesting a potential positive effect on the vascular system during training since cGMP acts as a second messenger producing smooth muscle relaxation and vasodilation. However, the level of other biomarkers changed. Juice supplementation and physical exercise decreased the plasmatic levels of 8-hydroxyguanine, which suggests a positive effect against DNA oxidation, and also decreased the level of urinary 8-isoprostaglandin F2α, a urinary lipid oxidation biomarker. Chronic exercise, independently of juice supplementation, also decreased another DNA oxidation product, 8-hydroxy-2′-deoxyguanosine. On the other hand, 5% aronia-95% citrus juice intake increased 8-nitroguanosine, indicating a participation of the constituents of the juice in increased redox activity. Indeed, hesperidin (characteristic from citrus juice) is a phenolic compound containing hydroxyl groups that may generate ROS through autoxidation. Due to these contradictory results, the authors are developing further research to clarify the positive influence that the intake of functional fruit juices and polyphenols could have on athletes (Garcia-Flores et al., 2016a).

F4-Neuroprostanes originate from docosahexaenoic acid peroxidation, an essential constituent of nervous tissue that is highly enriched in neurons and is highly susceptible to oxidation. F2-Dihomo-isoprostanes are specific markers for free radical-induced adrenic acid peroxidation, being potential markers of free radical damage to myelin in the human brain. Regarding CNS-associated oxidative stress, biomarkers related with neuronal membrane degradation (10-epi-10-F4t-neuroprostane and 10-F4t-neuroprostane) and with neuromotor system degradation (17-epi-17-F2t-dihomo-isoprostane, 17-F2t-dihomo-isoprostane, ent-7(*R*)-7-F2t-dihomo-isoprostane, and ent-7-epi-7-F2t-dihomo-isoprostane) were quantified in athletes' urine by UHPLC-QqQ-MS/MS. The F4-neuroprostanes were not detected after the consumption of 5% aronia-95% citrus juice and all F2-dihomo-isoprostanes, except ent-7-epi-7-F2t-dihomo-isoprostane, decreased in the juice-supplemented group. Overall, these results showed that the chronic intake of this polyphenolic rich juice plus adequate training influenced the oxidative/nitrosative status of the CNS in young adult triathletes, which will help to elucidate novel interactions and mechanisms between excretion of lipid peroxidation metabolites, supplementation of polyphenols-rich juice in the diet, and physical exercise during a training season (Garcia-Flores et al., 2016b).

Besides triathletes, clinical studies are also being conducted with metabolic syndrome patients. Using ELISA and colorimetric assays, Mulero et al. (2012) and Bernabé et al. (2013) assessed the influence of 5% aronia-95% citrus juice on oxidative stress biomarkers present in urine and blood samples from metabolic syndrome patients. Twenty healthy persons (control) and eighteen patients consumed 300 mL of juice on a daily basis during 6 months. In other group (15 patients), the juice was replaced by a placebo beverage. Taking into consideration the beneficial effect of the juice on the level of most of the biomarkers tested (15-isoprostane F2t, reduced/oxidized glutathione (GSH/GSSH), protein carbonyl groups, 8-hydroxydeoxyguanosine, HDL, LDL, oxidized LDL, glucose, cholesterol, triglycerides, C-reactive protein, and homocysteine) at the end of the 6 months, the authors concluded that antioxidant supplementation may be a good candidate for protecting against oxidative stress and development of cardiovascular disease in metabolic syndrome patients.

Several other studies showed that fruit and vegetable juices rich in phenolic compounds, carotenoids, betalains, and vitamin C (e.g., orange, apple, acai, cranberry, tomato, sweetie fruit, pomegranate, guava, cherry, purple grape, beetroot, and carrot) affect cardiovascular risk factors in healthy and hypertensive individuals, such as lowering blood pressure and improving blood lipid profiles. The main mechanisms of action through which these juices act in the organism includes, among other factors, their antioxidant effects, their improvement of the aspects of the cardiovascular system, inhibition of platelet aggregation, anti-inflammatory effects, and prevention of hyperhomocysteinemia (Zheng et al., 2017).

12.4 The Effect of Processing on the Content of Bioactive Compounds

Several factors affect the chemical composition and bioactivity of fruit juices, namely, storage temperature, heat treatments, pasteurization, drying processes, enzymatic treatments, etc. Ascorbic acid stability in some beverages during their shelf-life was also evaluated. Degradation of about 54% was observed in a tea drink (de Quirós et al., 2009). The stability of vitamin C in tomato juice seems to be affected by the type of container. The use of glass containers non-protected from light leads to the lowest concentration of ascorbic acid and total vitamin C when compared to other packaging materials (Sánchez-Moreno et al., 2006).

12.4.1 Drying Processes

Lee et al. (2013) compared the ascorbic acid, TPC, and betacyanin content and antioxidant activity using the ABTS assay of red and white dragon fruit juices untreated and submitted to spray drying. The spray drying process induced changes in ascorbic acid (from 14.8 to 11.7 mg/100 g) and betacyanin content (196 to 58.8 mg/L) in red dragon fruit. On the other hand, the TPC was reduced for both species (17.8–6.1 for red dragon fruit and 7.5–2.2 mg/100 g for white dragon fruit) as well as the antioxidant activity (ABTS method). In addition, storage of both dragon fruit powders at 25°C for 25 days with increasing relative humidity at 43%, 54%, or 75% resulted in caking and structural collapse with liquefaction but no visible changes were observed when powders were stored at 33% relative humidity. Apart from the structural changes, storage did not influence the antioxidant activity and bioactive compound contents.

Goldenberry (*Physalis peruviana* L.) is an exotic fruit with antioxidant activity. In order to preserve the bioactive contents, freeze-dried microencapsulation was performed using maltodextrin mixed with gum arabic, alginate, and pectin in different proportions (10:0, 9:1, 8:2) and core to coating ratios (3,10) (Dag et al., 2017). Concerning the phenolic compounds identified in the freeze-dried powder, 5-*O*-caffeoylquinic acid, *p*-coumaric acid, and ferulic acid were the main compounds, while gallic acid, caffeic acid, quercetin, myricetin, and kaempferol were present in trace amounts (Table 12.2). Microencapsulation proved to be a good choice to preserve the phenolic compounds since freeze-dried goldenberry juice had higher antioxidant activity (through DPPH assay) than fresh goldenberry juice. Overall, the microencapsulated goldenberry juices with 9:1 and 8:2 maltodextrin: pectin ratio were shown to be the best formulations due to higher encapsulation efficiency and antioxidant activity. Finally, using an in vitro digestion system it was possible to conclude that the release of phenolic compounds from microcapsules was higher in simulated intestinal fluid than in gastric medium.

12.4.2 Cold Plasma

Cold plasma is an emerging technology that has been recently applied in many biological treatments including sanitization and surface modification. Briefly, it is an ionized gas (carbon dioxide, argon, nitrogen, helium, oxygen, or air) characterized by active particles such as electrons, ions, free radicals, and atoms that are both in ground and excited states at ambient temperature. The ROS and RNS generated in the gas plasma such as $^{\bullet}NO$, NO_2^-, NO_3^-, $ONOO^-$, OH^-, $^1O_2$, O_3, and H_2O_2 have a direct effect on microbial inactivation and surface treatment of packing materials (Rodríguez et al., 2017). These authors (Rodríguez et al., 2017) investigated the effect of cold plasma (N_2) application (N_2 flow—10, 30, and 50 mL/min; and treatment time—5, 10, and 15 min) on vitamin C, antioxidant activity (FRAP, DPPH, and ABTS), TPC and TFC, and sugar profiles of cashew apple juice. Comparing to the untreated sample, increments of vitamin C were observed at the N_2 flow rate of 10 mL/min (5 and 10 min), but then decreased to lower values than the control, and was minimal at 50 mL/min (15 min). The authors hypothesized that at 10 mL/min, the rate of regeneration of ascorbic acid by the ascorbate-glutathione cycle is greater than the rate of its decay through its reaction with the generated reactive species. Conversely, stronger conditions favored the release of polyphenols and flavonoids. The TPC value was maximum at 50 mL/min and increased with increasing exposure time, while the highest TFC value was achieved at 30 mL/min (15 min), showing that flavonoids required less energy than polyphenols to be released from its bound forms. The activity measured by FRAP showed a pattern similar to those of TPC and TFC profiles, while vitamin C was the main contributor to DPPH scavenging activity. Regarding sugars, sucrose was minimal at 10 mL/min and equal or higher than the control at 30 and 50 mL/min, which could be related to the higher degradation of the oligosaccharides present in the juice with a high degree of polymerization into sucrose. Conversely, the reducing sugars fructose and glucose exhibited a general degradation pattern regardless of the plasma treatment.

12.4.3 Storage Temperature

Arena et al. (2001) analyzed the anthocyanin content and the antioxidant activity through ABTS of 17 freshly squeezed and processed and commercial blood and blond orange juices by spectrophotometric assays as well as ascorbic acid and hydroxycinnamic acids by HPLC. Processed and commercial samples were composed of non-concentrated or reconstituted from concentrated juices to the same Brix of the corresponding non-concentrated juices. Anthocyanins content was strongly variable among samples reaching its maximum at 104 mg/L (reconstituted processed juice). Ascorbic acid content ranged from 262 (non-concentrated commercial sample) to 669 (freshly squeezed) mg/L, while those of sinapic, caffeic, ferulic, and coumaric acids were, respectively, 6.7–15.1 mg/L, 3.2–7.5 mg/mL, 30.1–44.2 mg/mL, and 7.4–26.5 mg/L. In general, the higher content of these compounds was found in processed samples, followed by squeezed juices and commercial samples, and all blood orange juices were richer than blond orange ones. Three of the freshly squeezed blood orange juices showed the highest total antioxidant activity values. Moreover, reconstituted processed blood juices presented higher total antioxidant activity than non-concentrated juices, and the difference could be due to the increased amount of carotenoid pigments in the reconstituted samples, as a consequence of the thermal concentration process. Despite the degradation of anthocyanins during storage, the total antioxidant activity of processed and commercial juices remained unchanged up to 60 days at 2°C, whereas it decreased when reconstituted juices were stored at 20°C, in accordance with the observed decrease of ascorbic acid in the same conditions.

12.4.4 Thermal Treatments

Ordóñez-Santos et al. (2017) determined the effect of ultrasound treatment on the color and bioactive compounds of Cape gooseberry juice. The juice was divided into five samples: control, heat pasteurization, ultrasonic for 10 min, ultrasonic for 20 min, and ultrasonic for 40 min. Ascorbic acid content decreased in all samples affected by ultrasound or heat treatment when compared to control, probably due to oxidation processes generated during heat and ultrasonic treatments. On the other hand, TPC, β-carotene, α-carotene, β-cryptoxanthin, zeaxanthin, and lycopene increased with increasing sonication treatment times. The increase of the phenolic compounds in the samples treated with ultrasound in comparison to the control and heat treatment is possibly due to the greater disruption of the cell walls, facilitating the release of bound phenolic to the pectin, cellulose, hemicellulose, and lignin traces of the cell wall. In a similar way, the increase of the carotenoids in the juice processed by ultrasound could also be explained by mechanical rupture of the cell wall, allowing the release of these compounds, together with the inactivation of the enzyme lipoxygenase due to the processes of cavitation. A significant decrease in TPC was observed in juice processed by pasteurization when compared to control, probably because thermal heating in fruit juices generates complex physical and chemical reactions affecting the phenolic composition, including the release of phenolic compounds from their bonded forms, the degradation of polyphenols, and the breakdown and transformation of phenolics.

12.4.5 Enzymatic Treatment

The cantaloupe juice was submitted to a combined treatment of Rapidase EX color (pectolytic enzyme) and Accellerase 1500 (cellulase) in order to release bioactive compounds. The ascorbic acid content was analyzed using HPLC, the control sample containing 120 mg/L of ascorbic acid (Table 12.3). Increasing the enzyme concentration (0.25%–1.00%) and the duration of the treatment (1–5 h) had positive and negative impacts on the ascorbic acid content, respectively. Indeed, at 1% enzyme concentration, ascorbic acid varied from 317 mg/L at the end of 1 h to 271 mg/L at the end of 5 h. The highest β-carotene content was obtained at the end of 3 h with 1% enzyme concentration (145 μg/100 mL), and TPC and TFC tended to increase with increasing concentrations of enzymes and were maximum at the end of 4 h (138 mg GAE/mL and 110 mg quercetin-3-*O*-rutinoside/mL) and 5 h (110 mg quercetin-3-*O*-rutinoside/mL), respectively. The antioxidant activity assessed by the DPPH and FRAP assays also increased until 3 h of treatment, but then decreased, which coincided with the reduction in both vitamin C and β-carotene during prolonged incubation time (Naknaen, 2017). These results showed that the enzyme mixture facilitated cell wall components rupture, which enhanced the recovery of bioactive compounds.

The effect of pasteurization (85°C for 30 s) on the profile of bioactive compounds and antioxidant capacity of a fermented orange juice was studied (Escudero-López et al., 2016). Ascorbic acid (203 mg/L), total flavanones (647 mg/L), total carotenoids (7.07 mg/L), and provitamin A (90.06 RAEs/L) values of pasteurized orange beverage were lower than those of fermented juice while total phenolic (585 mg/L) remained unchanged. Pasteurization also produced a decrease in the antioxidant capacity of fermented juice although the values obtained for ABTS and ORAC were similar to the original non-fermented juice.

12.4.6 Alcoholic Fermentation

Since the intake of bioactive compounds and moderate alcohol decreases the risk of cardiovascular diseases, Escudero-López et al. (2013) studied the influence of controlled alcoholic fermentation (using the yeast strain *Saccharomycetaceae* var. *Pichia kluyveri*, at 20°C for 15 days) on the bioactive compound profile of orange juice. Total and individual flavanones (determined using UHPLC-MS/MS) and carotenoids (using spectrophotometry and chromatography) significantly increased throughout the fermentation since the process enhanced the extraction of these compounds from the pulp. Ascorbic acid (determined using a titration method) did not undergo a significant change but the TPC (using the Folin-Ciocalteu method) decreased. Concerning the antioxidant capacity, ABTS and FRAP values stayed constant during the course of the process but ORAC and DPPH scavenging activity significantly increased. Therefore, the results suggest that alcoholic fermentation has a positive effect on antioxidant content and activity of orange juice.

Chemical and biological characterization of eight *Vitis labrusca* juices—white or purple- from organically or conventionally grown grapes was performed by Dani et al. (2007). Purple juices were heat-extracted using pulp, seeds, and skin, while the skin was removed before extraction from white grapes. Commercial conventional juices were manufactured using heat extraction (approximately at 50°C), with a subsequent pressing step in order to separate the pulp, and then submitted to pasteurization (at 85°C). The other purple and white juices were manufactured using heat extraction, immediately followed by bottling, both at 80°C. Using spectrophotometric and chromatographic methods, the authors showed that organic grape juices showed higher values of total polyphenols, resveratrol, and anthocyanins (cyanidin, delphinidin, peonidin, and malvidin) than the conventional grape juices, and purple juices presented higher total polyphenol content in comparison with the white grape juices (Table 12.2). Finally, purple juices presented higher catechin and epicatechin contents as compared to white juices. Four procyanidins (B1–B4) were identified in all samples, with B3 being in higher amounts. Concerning the antioxidant activity assessed using the DPPH method, serum lipid peroxidation inhibition, and superoxide dismutase and catalase-like activities, purple juices also displayed stronger activities as compared to white juices, which can positively be correlated with total polyphenol content.

12.5 Conclusions

The production and consumption of functional foods, which includes beverages, has gained increased importance, as they provide a health benefit beyond the basic nutritional functions, leading to consumer demands.

Fruits contain a wide range of health-promoting components, including phenolics, carotenoids, betalains, and ascorbic acid, among others. However, nowadays people do not consume sufficient amounts of fruits, so the introduction of different formats of fruit-derived foods and beverages can help to increase the total consumption of fruit components.

The qualitative and quantitative analysis of bioactive composition is a requirement for product development and quality control in order to verify health content claims. Thus, it is imperative to analyze the composition and amounts of bioactive compounds before adding them to foods, after processing and during storage time. The range of analytical methodologies available (UV-Vis spectrometry, electrochemistry, and chromatography) depends on the type of bioactive compounds under target.

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13

PLANTS INFUSED WATER AS PREFERRED HEALTHY DRINKS

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13.1 Introduction

Water infusion involves immersion of plant material in water or boiling water for a certain period of time to extract its phytochemicals and flavors. The resulting mixture will then be filtered using either a filter or siever. The filtrate is also known as an infusion. Thus, an infusion is a mixture of phytochemicals and flavors. Phytochemicals are chemical products of photosynthesis. They can be categorized into primary metabolites, secondary metabolites, and biopolymers. Examples of primary metabolites are monosaccharides, disaccharides, organic acids, and amino acids. On the other hand, phenolics and essential oils are secondary metabolites while proteins, lipids, and polysaccharides are biopolymers (Saldaha et al., 2017).

Fruits, vegetables, and herbs are common plant materials used for the preparation of infused water. They exist in variety of colors with different flavors and nutritious compounds. They are commonly used as raw ingredients in our diets. Fruits such as orange, banana, grape, and lemon are the mature ovaries of flowering plants, while vegetables such as okra, carrot, pea, lettuce, tomato, cabbage, pepper, and chili are edible parts of plant such as leaves, stems, and roots. Moreover, herbs are leaves, flowers, or seeds of any herbaceous plant. Examples of herbs are basil, celery, garlic, mint, thyme, cumin, and arrowroot. Most of the fruits, vegetables, and herbs are only grown in certain countries due to the environment temperature, humidity, and specific time/season of the year. These factors may also affect the nutritional qualities. Fruits, vegetables, and herbs mostly contain water (90%) once they are harvested. They are low in fat and carbohydrates, but rich in vitamins,

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minerals, and fibers (Rickman et al., 2007). The nutritional value of orange, okra, and basil has been reported to be approximately 86, 90, and 92 kcal per 100 g, respectively (Table 13.1) (USDA, 2016).

The recommended intake of fruits and vegetables is at least 400 g per day (WHO, 2003) while herbs are normally used in small quantity to enhance food flavors. Adequate intake of fruits and vegetables is needed to prevent chronic diseases and thus promoting body health. However, the consumption of fruits and vegetables by populations in Asian,

Table 13.1 Nutrient Composition of Orange, Okra, and Basil (USDA, 2016)

		Nutritional Facts, per 100 g		
Nutrient	**Unit**	**Orange, Raw**	**Okra, Raw**	**Basil, fresh**
Proximates				
Water	g	85.97	89.58	92.06
Calories	kcal	49	33	23
Protein	g	0.91	1.93	3.15
Total fat	g	0.15	0.19	0.64
Total carbohydrate	g	12.54	7.45	2.65
Dietary fiber	g	2.2	3.2	1.6
Sugars	g	8.50	1.48	0.30
Minerals				
Calcium, Ca	mg	43	82	177
Iron, Fe	mg	0.13	0.62	3.17
Magnesium, Mg	mg	11	57	64
Phosphorus, P	mg	23	61	56
Potassium, K	mg	166	299	295
Sodium, Na	mg	1	7	4
Zinc, Zn	mg	0.08	0.58	0.81
Vitamins				
Vitamin C	mg	59.1	23.0	18
Thiamin	mg	0.068	0.200	0.034
Riboflavin	mg	0.051	0.060	0.076
Niacin	mg	0.425	1.000	0.902
Vitamin B-6	mg	0.079	0.215	0.155
Vitamin E	mg	0.15	0.27	0.80

African, and most of Western countries is reported to be far less than the recommended intake (Peltzer and Pengpid, 2012). Low consumption of fruits and vegetables is one of the top 19 leading risk factors for chronic diseases. Lacking of fruits and vegetables in diets can increase the risk of chronic diseases such as cardiovascular diseases, ischemic heart diseases, stroke, cancer, obesity, and diabetes. The other major risk factors that cause death in the world are high blood pressure (BP; 13%), tobacco use (9%), hyperglycemia (6%), lack of exercise (6%), and overweight or obesity (5%). These risk factors affect all high-, middle-, and low-income groups from the world (WHO, 2009). The World Health Organization and Food Agriculture Organization (2003) projected that the burden of chronic disease would be increased to 57% by 2020.

However, these chronic diseases are mostly preventable. One of the methods to control the diseases is the use of commercialized medications but these might lead to undesirable side effects. Thus, plant infused water has the potential usage in controlling chronic diseases due to their reported health beneficial effects such as antioxidant, antidiabetic, anti-inflammatory, antihypertension, anticancer, and antibacterial. Past studies have shown that plant infused water exhibited antioxidant activity via free radical scavenging or ion reducing activity, thus subsequently preventing tissue injury or damage (Apak et al., 2006). This antioxidant activity can be determined using α,α-diphenyl-β-picrylhydrazyl (DPPH), 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) or oxygen radical absorbance capacity (ORAC), ferric reducing antioxidant power (FRAP), or cupric reducing antioxidant capacity (CUPRAC) methods (Apak et al., 2006; Atoui et al., 2005; Vaquero et al., 2010; Dalar and Konczak, 2013; Kaliora et al., 2014).

These beneficial properties of plants are mostly due to the presence of several phenolic compounds (flavones, flavanones, anthocyanins, isoflavones, and catechins) and antioxidants such as carotenoids (provitamin A), tocotrienols and tocopherols (vitamin E), and ascorbic acid (vitamin C) (Álvarez et al., 2016). In addition, different bioactive compounds may exhibit different beneficial efficiencies in different food systems due to their molecular and polarity characteristics (Mohd Azman et al., 2016). In nutraceutical industries, these bioactive compounds are often utilized as food additives or supplements in preparing functional foods (Álvarez et al., 2016). This suggests that plant infused water with these bioactive compounds could be consumed as preferred healthy drinks without bringing side effect as it is made from natural sources, unlike the medicinal pills. Therefore, the present chapter outlines the water extraction of phytochemicals as well as the beneficial properties of infused water from various parts of fruits, vegetables, and herbs (Fig. 13.1).

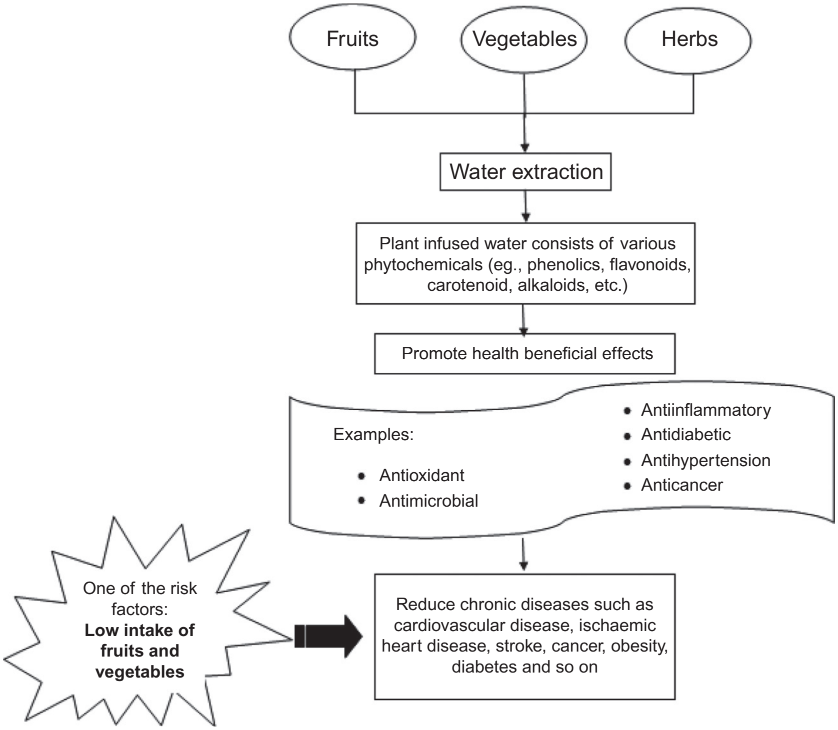

Fig. 13.1 Plant infused water in relation to body health.

13.2 Water Extraction of Phytochemicals

Phytochemicals or natural compounds from plant material can be extracted in many ways. Extraction is a method to separate the valuable and beneficial components from mixture of solid or liquid medium (Doughari, 2012). Numerous methods used in extraction of bioactive components from plants are shown in Fig. 13.2. These include infusion, decoction, maceration, solid-phase, steam or hydrodistillation, pressing, percolation, Soxhlet extraction, supercritical fluid extraction (water or CO_2), ultrasonic, microwave, and pulsed electrical field extraction (Doughari, 2012).

Numerous researches have been using organic solvents as extraction method on fruit (Isabelle et al., 2010; Masci et al., 2016). Water is also known as green extraction solvent and is remarkably limited (Pongnaravane et al., 2006; Rangsriwong et al., 2009; Vergara-salinas et al., 2013). However, water has been widely employed due to its unique physicochemical properties in retaining liquid state from ambient to near critical conditions at high temperature and pressure (Castro-Puyana et al., 2017). A hot or subcritical water extraction (SWE) is usually applied in the current extraction of phytochemicals in

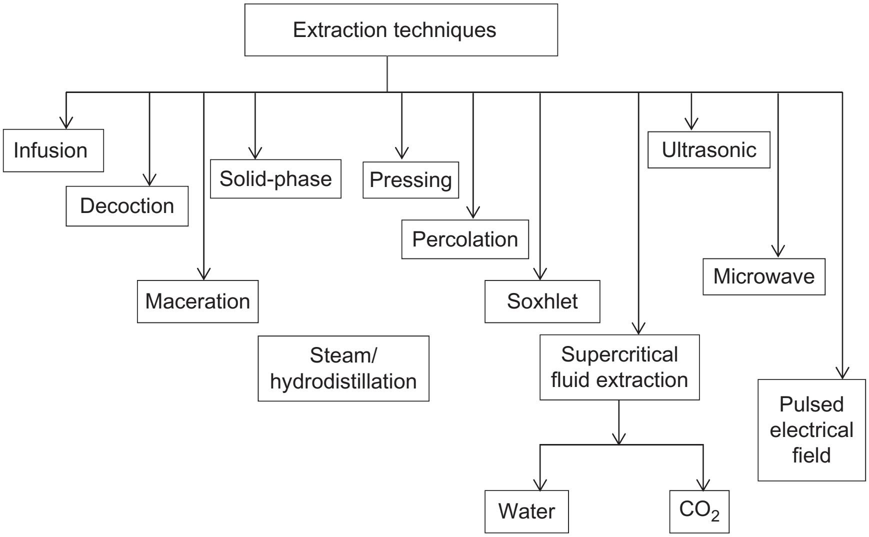

Fig. 13.2 Different techniques of extraction.

plant materials such as fruits, vegetables, and herbs. This pressurized water under subcritical conditions with low polarity can solubilize both nonpolar (at high temperature) and polar (at low temperature) organic compounds such as phytochemicals. This is because phytochemicals are generally insoluble in water at ambient temperature (Kiamahalleh et al., 2016).

It is a trend nowadays to incorporate natural plant materials and water as a beneficial beverages or drinks in regards to the great possibility of obtaining health beneficial phytochemicals extracted from plant materials with hot water or pressurized hot water. Healthy drinks prepared from infused water with fruits, vegetables, or herbs are the most common and conveniently prepared beverages by steeping the plant materials in the hot water suspension (boiled or at a certain appropriate temperature) for a period of time. The strained liquid of the infused plant materials can be consumed fresh directly, refrigerated, or bottled for longer shelf life and future use. By using this infusion technique, the bioactive ingredients of plant materials can be dissolved and released easily in the water. The duration of steeping time is greatly depended on the intention of usage or expected result. It could be for creating optimum flavor or achieving the highest plant extracts yield or health benefits. Therefore, various experimental preparatory works and practices have been researched to acquire the optimum results for both objectives. Theoretically, extraction of each sample can be optimized with appropriate extraction parameters. Besides herbs, fruits such as lemon and apple, or vegetables may be used to prepare healthy drinks using infused water. Furthermore, combination of herbs, fruits, and vegetables is also popular in the preparation of this natural infused water. The subsequent subtopics elaborate more on the findings and possible optimum conditions for water extraction of phytochemicals from fruits, vegetables, and herbs.

13.2.1 Fruits

Fruits contain great amount of phytochemical compounds with high antioxidant activity such as ascorbic acid, carotenoids, α-tocopherol, flavonoids, and phenolic compounds. Previous study was conducted by Aamer (2016) to compare the extraction methods used in preparing aqueous extract of nutritional doum fruit. Hot water infusion of the dried doum fruit pulp is also known as doum drink has been widely consumed by Kenyans as a health tonic to reduce hyperlipidaemia, atherosclerosis, and glomerulosclerosis in the Turkana region (Martin, 1999; Cook et al., 2000). In one of the methods, the crushed doum fruit was soaked in water at a ratio of 1:5 (*w*/*v*) at ambient temperature (22 ± 2°C) for 4, 8, and 12 h. Another method was by boiling the crushed doum fruit in water at a ratio of 1:5 (w/v) for 5, 10, and 15 min. Vitamin B compounds, total antioxidant activity, total phenolic, and flavonoid contents of doum fruit drink were determined by high-performance liquid chromatography. The obtained data exhibited that the most preferable fruit extracts were prepared by both methods with soaking at ambient temperature (22 ± 2°C) for 8 h and by boiling for 10 min. The process flow of preparing the doum fruit extract is displayed in Fig. 13.3.

Andrianto et al. (2017) conducted extraction of *Phyllanthus acidus* using ethanol and water as extraction solvent. The extraction treatments are by using absolute ethanol, 70% ethanol, 30% ethanol, and water. Qualitative phytochemicals tests were carried out to determine potential secondary metabolites (tannins, alkaloids, saponins, flavonoids, phenolics, terpenoids, glycosides, and steroids) contained in *Phyllanthus acidus* fruit. In addition, the optimum water temperature and soaking time for production of a smooth kokum pulp was determined by Bafna (2012) using a response surface methodology. Kokum pulp was extracted using water extraction method. Different water extraction temperature from 13°C to 33°C and duration from 10 to 50 min were employed to extract kokum pulp. An increase in soaking time and water temperature used for extraction of pulp resulted increase in pulp recovery and hydroxy citric acid content of the kokum pulp but to a certain level. Optimum conditions for the formation of smooth kokum pulp were concluded to be using water at 24.97°C and soaking time of 30.42 min.

Extraction of immature fruits such Japanese pear (*Pyrus pyrifolia*), peach (*Prunus persica*), blueberry (*Vaccinium corymbosum*), grape

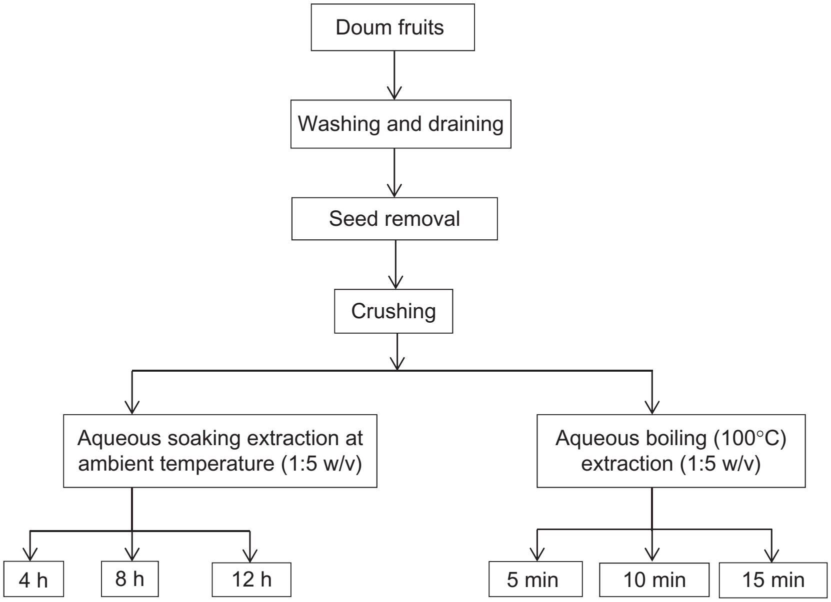

Fig. 13.3 Process flow of preparing the doum fruit extract.

(stem) (*Vitis vinifera*), grape (fruit) (*Vitis vinifera*), Japanese plum, (*Prunus thibetica*), Japanese persimmon (*Diospyros kaki*), quince (*Cydonia oblonga*), prune (*Prunus domestica*), green apple (*Malus domestica*), apricot (*Prunus armeniaca*), red apple (*Malus pumila*), European pear (*Pyrus communis*), and nectarine (*Prunus persica* var. *nucipersica*) was carried out by Heng et al. (2017) using a pressurized hot water extraction (PHWE) method at 100°C. The efficacy of this method was compared to the conventional reflux method. Among all the fruit extracts, grape (stem) extract contained the highest amount of polyphenol using the PHWE or reflux extraction. Polyphenols found in fruits are well correlated with the antioxidant activity (Isabelle et al., 2010; Shahidi et al., 1992). By using ORAC assay, results also showed that grape (stem) contained the highest antioxidant activity. Besides grape (stem), quince and Japanese persimmon also showed the highest total phenolic content (TPC) and antioxidant activity using the PHWE extraction.

Studies by Rangsriwong et al. (2009) investigated the effect of SWE of *Terminalia chebula* Retz. on several major polyphenolic compounds such as ellagic acid (EA), gallic acid (GA), and corilagin (CG) The extraction temperature was ranging from 120°C to 220°C, water flow rates were ranging from 2 to 4 mL/min and pressure at 4 MPa. The analyzed results obtained were compared to those extracts acquired from the Soxhlet extraction with ethanol and hot water extraction at ambient pressure. The highest amount of EA and GA was obtained when the subcritical water temperature was increased up to 180°C, while the highest amount of CG was achieved at 120°C.

Response surface methodology was conducted by Koyu et al. (2017) to optimize the SWE of black mulberry (*Morus nigra* L.) fruits. Spectrophotometry and liquid chromatography with tandem mass spectrometry (LC-MS/MS) analysis were carried out to determine the phenolics, flavonoids, and anthocyanins contents in the extracted black mulberry fruits. With the same duration (60 min) and water flow rate (2 mL/min), both extraction temperatures at 60°C and 120°C were optimum in producing extracts with IC_{50} value of 1.84 and 1.71 mg/mL, respectively. These two extraction conditions were able to produce extracts with stronger tyrosinase inhibitory activity compared to those of conventional solvent extraction method, with higher IC_{50} value of 2.81 mg/mL.

Subcritical water under pressure held at temperatures between 110°C and 160°C was employed by King et al. (2002) for the extraction of anthocyanin-based pigments from fruit berries in both wet and dry conditions. Fruit berries used in this study include raspberry, elderberry, chokeberry, and bilberry. Their associated stems, skins, and pomaces or by-products were also extracted for the anthocyanin determination and comparison.

Jujube fruit (*Ziziphus jujuba* Mill) leaf extract was found to contain active ingredients to soothe nerves and improves sleeping condition. Ever since the jujube fruit (*Ziziphus jujuba* Mill) leaf infusion is popular bedtime beverage, Damiano et al. (2017) investigated further the bioactive compounds of the aqueous extract of the jujube fruit leaf by analyzing the polyphenol content and their antioxidant activities. They have identified three major antioxidant polyphenols namely quercetin (QE), catechin, and gallocatechin in the leaves. Furthermore, their results further promoted the consumption of jujube leaf extract as a bedtime beverage by their new reported finding on the anticaries activity possessed by the extracts.

Furthermore, Xu et al. (2008) studied the mineral content and phenolic compounds of the citrus fruit peel. Two varieties of citrus fruit were selected, namely Satsuma mandarin and Ponkan with scientific name of *Citrus unshiu* Marc. and *Citrus poonensis* Hort. ex Tanaka, respectively. They have been used as traditional medicines or seasonings in Chinese cooking in the name of chenpi. The samples were prepared by mixing citrus peel powder with 100 mL of boiling water and let to infuse for about 30 min. Ponkan showed much greater content of phenolic acids, flavanone glycosides, and polymethoxylated flavones compared to Satsuma mandarin in the hot water extract. By using atomic absorption spectrometry, three major elements such as magnesium (Mg), calcium (Ca), and potassium (K) and four trace elements, namely copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) were analyzed and the peel has the highest amount of K followed by Ca and Mg. They also suggested that the maximal extraction of phenolic compounds and minerals from citrus peels can be obtained by two times extraction at 100°C for 30 min.

Another phytochemical screening was conducted by Agbafor and Nwachukwu (2011) on velvet bean (*Mucuna pruriens*) and black plum (*Vitex doniana*) in Nigeria. The results showed that aqueous and ethanol extracts of *Mucuna pruriens* and *Vitex doniana* contained saponins, tannins, anthraquinones, terpenoids, and flavonoids. However, results also discovered that only the extracts of *Vitex doniana* contained alkaloids, while cardiac glycosides were detected in the extracts of *Mucuna pruriens* only.

13.2.2 Vegetables

Besides fruits, vegetables are high in vitamins, minerals, essential oils, fiber, and phytochemicals, but low in calories and fat (Banerjee et al., 2012). They are one of the essential food categories in human diets to maintain the overall health conditions of human body system and prevention of diseases. The phytochemicals such as phenolics, carotenoids, lignans, and lycopenes have been proven to possess health beneficial properties such as anti-allergic, anti-inflammatory, antitumor (Norhanom et al., 1999), antimicrobial, and antithrombotic (Asif and Khodadadi, 2013; Mushtaq and Wani, 2013). The antioxidant capacities derived from phenolic compounds are believed to bring potential health effect by consumption of vegetables (Nagavani and Rao, 2010; Shiban et al., 2012).

However, the content of phytochemicals in plant materials is greatly affected by the variation of cultivar, growing conditions, cultivation methods, maturity stages, processing techniques, and storage conditions (Naczk and Shahidi, 2006). For instance, an increase of furanocoumarins level from 1 to 33 mg/kg fresh weight was found in whole parsnips that were stored at 4°C for 7 days. However, there was only a little effect on the furanocoumarins content in parsnips stored at −18°C up to 50 days (Ostertag et al., 2002). Moreover, different processing techniques such as chopping, peeling, boiling, frying, and microwaving may reduce the total content of QE conjugates in onions. Reduction of QE conjugates by 1% was indicated in the chopped onions, while a reduction of QE conjugates up to 75% was occurred in water boiled onions (Gennaro et al., 2002; Makris and Rossiter, 2001).

Numerous studies on water boiled vegetables and vegetables infused water were conducted in various countries in the world. A team of researchers in Taiwan led by Kao et al. (2014) evaluated the effects of boiling water on the TPC, total antioxidant capacity, and total carotenoid content (TCC) of four types of carotenoid-rich green leafy vegetables.

The vegetables used in this study include Thai basil leaves, cilantro, choy sum (Chinese flowering cabbage), and sweet potato leaves. The duration of boiling time was ranged from 0 to 30 min. The results showed that the TCC of 10 min boiled cilantro, 5 min boiled sweet potato leaves, and 5 min boiled Thai basil leaves achieved the maximum content compared to the other durations of boiling time. However, 30 min of boiling did not affect the TCC of choy sum compared to the other durations of boiling time. A significant ($P < 0.05$) increase of TPC was reported in Thai basil leaf and sweet potato leaf that were boiled for 1 and 5 min, respectively. However, a negative effect on the TPC was found in boiled cilantro and choy sum. Their findings concluded that a boiling time of 5 min can preserve or increase TCC, TPC, and total antioxidant capacity for these four vegetables.

Antioxidant properties of aqueous extracts of dried persimmon leaves obtained from different drying methods and different infusion conditions were investigated by Heras et al. (2014). The drying methods include shade drying, freeze drying, and hot air drying at 100°C and 180°C. The dried persimmon leaves were infused at 70°C, 80°C, and 90°C for 1, 3, 5, 60, and 1440 min. Their findings suggested that the optimum process to obtain stabilized persimmon leaves in terms of total flavonoid content (TFC), TPC, and antioxidant activity is by hot air drying at 100°C. In addition, infusion condition at 90°C for 60 min can maximize the antioxidant compounds extraction and was suggested to be the optimal conditions of aqueous extraction for dried persimmon leaves.

A team of researchers in Malaysia led by Huda-Faujan et al. (2015) conducted a study to assess the antioxidant activities and TPC of aqueous and ethanolic extracts of Malaysian traditional vegetables. Eight samples of Malaysian traditional vegetables namely *Anacardium occidentale* shoot, *Carica papaya* shoot, *Curcuma longa* leaves, *Etlingera elatior*, *Manihot esculenta* shoot, *Pithecellobium jiringa*, *Psophocarpus tetragonolobus*, and *Sauropus androgynus* were used in this study. Their local names are known as pucuk gajus, pucuk betik, daun kunyit, bunga kantan, pucuk ubi, jering, kacang kelisa, and cekur manis. The TPC of water extracts using Folin-Ciocalteu assay was ranged from 7.08 to 14.76 mg gallic acid equivalent (GAE).

In Nigeria, a research team led by Ikewuchi et al. (2017) carried out a screening test for the presence of bioactive molecules in an aqueous leaf extract of herbaceous waterleaf (*Talinum triangulare*) using gas chromatography coupled with pulse and flame ionization detectors. They had discovered the presence of high carotenoids content, moderate level of benzoic acid derivatives, flavonoids, and hydroxycinnamates and low levels of alkaloids, terpenes, glycosides, saponins, phytosterols, allicins, and lignans. They have detected 10 carotenoids comprising of 50.42% carotene and 33.30% lycopene, 9 benzoic acid derivatives with 84.63% ferulic acid and 11.92% vanillic acid, and 6 hydroxycinnamates with 55.44% *p*-coumaric acid and 44.46% caffeic acid. Moreover, 30 flavonoids comprised of 50.35% QE and 39.36% kaempferol were found from this screening test. From all the eight lignans detected, retusin contributed to 88.02% of the total lignans.

A research on aqueous extraction of flower vegetables was conducted in Thailand by Krasaekoopt and Kongkarnchanatip (2005). Three kinds of Thai traditional flower vegetables namely *Sesbania grandiflora*, *Telosma minor*, and *Senna siamea* were selected for this research due to its high content of flavonoid, anthraquinone, and glycoside. Crude flavonoid was separated by using the column chromatography and found that flowers of *Senna siamea*, *Sesbania grandiflora*, and *Telosma minor* consisted of 8.6%, 8.4%, and 3.4% of flavonoid, respectively.

Optimum extraction conditions for aqueous extraction of curcumin from turmeric rhizome were investigated by Kiamahalleh et al. (2016). Curcumin (*Curcuma longa* L.) is a highly valuable polyphenolic component of turmeric and consisted of 2%–5% of total rhizome content. Effects of extraction temperature, retention time, pressure, and particle size on the yield of extraction were studied. SWE with pressure of 10 bar, particle size of 0.71 mm, retention time of 14 min, and extraction temperature of 140°C was employed to give a maximum weight percent of curcumin extracts at 3.8%. In addition, the yield of curcumin extraction was more than 76% in relation to the maximum curcumin content of total turmeric rhizome content at 5%.

13.2.3 Herbs

Herbs are mainly referred as valuable herbaceous plants with their savory, aromatic, and medicinal qualities. Herbs with medicinal qualities can be known as medicinal plants. They have been used for centuries due to their curative or preventative properties against various illnesses. One of the ways to consume herbs is by an infusion of herbs in water or herbal infusion (Apak et al., 2006; Vaquero et al., 2010).

Herbal infusion is one of the commonly consumed beverages worldwide due to its richness of polyphenolic compounds. It can be prepared using any part of the herbs, either the dried or fresh form of leaves, flowers, seeds, berries, roots, or bark by immersing them in water for an optimal time period (Apak et al., 2006; Vaquero et al., 2010). Different water temperatures used may influence the concentration of phenolic compounds in an herbal infusion, including the flavan-3-ol monomers. Higher TPC and TFC were found when boiling water was used (100°C) for preparing infusion. A common example of plant material used in herbal infusion is *Camellia sinensis* leaf. It is also known as green or black tea (BT) in Asian countries and is preferred by Chinese, Japanese, and Korean as their drinking beverages. A *Camellia sinensis* leaf infusion demonstrated high TPC and TFC when the leaves were prepared with water at 100°C (Horžić et al., 2009). Other than that, some of the geographical regions are rich in a diversity of flora species, including a variety of herbs which could be used for infusion. These herbs may consist of different phytochemicals and exert beneficial effects to human health.

Phenolic acids of nine herbal infusions (Greek mountain, mint, chamomile, dictamnus, eucalyptus, sage, linden, black Ceylon tea, and Chinese green tea) that were commonly found in the Mediterranean region were detected using diode array detection (DAD) in combination with positive electrospray ionization (ESI^+) mode mass spectrometry (LC-DAD MS). Among the nine herbal infusions, black Ceylon and green teas showed the highest TPC. Mint and dictamnus infusions were found to consist of flavanones, isoflavones, and flavones. Meanwhile, flavonols were also detected in dictamnus infusion. In addition, flavones and flavonols were found in sage and eucalyptus infusions, respectively. This shows that herbal infusion could be one of the major sources of polyphenols (Atoui et al., 2005).

In Eastern Anatolia at Turkey, tolik, nergiz, calba, and baresa spi are commonly used to treat stomachache while giyamambel and masicerk are used for anti-hyperglycaemic and hemorrhoids, respectively. Dalar and Konczak (2013) reported that the highest concentration of total phenolics was observed in the infusions of giyamambel, followed by masicerk, calba, baresa spi, and tolik and the lowest in nergiz infusion. In another study conducted by Vaquero et al. (2010), Yerba mate, lippie, and mint were reported with the highest concentration of total phenolic compounds among the 13 Argentinean herbal infusions. The TPCs of the infusions were ranged from 830 to 925 mg GA/L and showed more flavonoid fractions compared to non-flavonoid fractions (Vaquero et al., 2010).

Other than flavonoids, tannins and alkaloids were also found in herbal infusion of oak leaves from four different species (*Quercus resinosa, Q. grisea, Q. laeta*, and *Q. obtusata*) that are found in Mexico forest. They are commonly used in treating gastrointestinal and respiratory problems. All of them were found to contain hydrolysable tannins except *Q. obtusata*. Proanthocyanidins, the highest content of condensed tannins was detected in *Q. obtusata* infusion. These condensed tannins have the capability to decompose to anthocyanidin through oxidation. Other than *Q. obtusata*, the other three species of oak leaves were found with cardiac glycosides (Sánchez-Burgos et al., 2013).

Herbal infusions also possessed different minerals such as Ca, Mg, sodium (Na), and K. Calcium is the main component for bone and teeth development which is also important in regulating BP together with the presence of Mg. Meanwhile, Na and K are required for the body system regulation. All of these elements are known as essential minerals for the body health (Malik et al., 2013).

In the study by Özcan et al. (2008), the authors reported that the highest content of Ca and Mg was found in herbal infusion of senna leaf (*Casia anguistifolia*; 28.621 mg/100 mL) and basil (*Ocimum* basilicum; 16.230 mg/100 mL), respectively. In addition, herbal infusion of tarragon (*Artemisia dracunculus*) showed the highest contents of K (231.390 mg/100 mL) and phosphorus (P) (24.857 mg/100 mL). Malik et al. (2013) also reported that Ca and Mg were detected from aloe leaves (*Aloe vera*; 547.24 ± 11.10 mg/L) and ginkgo leaves (*Ginkgo biloba*; 103.987 ± 1.175 mg/L), respectively. Furthermore, the hibiscus petals were reported with the topmost concentration of some essential minerals such as Cu, Fe, P, K, Mn, Zn, nickel (Ni), and boron (B).

In Thailand, jiaogulan (*Gynostemma pentaphyllum*) and green tea (*Camellia sinensis*) are commonly used by Thais as their daily beverages. Jiaogulan has been reported with the pharmacological activities such as alleviation of asthma, respiratory disorders, and gastric ulcer; while green tea has antioxidant property. Jiaogulan and green tea are also found to have anti-hypercholesterolemic and anticancer effects. These herbs also consisted of different essential minerals. High concentration of Ca (jiaogulan: 26,805 μg/100 mL; green tea: 335.8 μg/100 mL) and Mg (jiaogulan: 7015 μg/100 mL; green tea: 1414 μg/100 mL) was found in the herbal infusions prepared from 2 g powder form of jiaogulan and green tea, respectively. However, the percentage of Ca released into the infusions was lower compared to the dried and ground herbs powder. The percentage of Ca released into the infusions from the powder form of green tea was 3.66%, but jiaogulan powder showed a better release of Ca with 64.22%. Moreover, the highest content of Fe and Zn was also found in jiaogulan (Fe: 125–2321 mg/kg; Zn: 46.26 mg/kg) and followed by green tea (Fe: 20–318 mg/kg; Zn: 32.17 mg/kg). Other micro-essential elements such as vanadium (V), chromium (Cr), and cobalt (Co) were also found at the highest concentrations in jiaogulan infusion, while green tea infusion has the highest concentration of Ni (Nookabkaew et al., 2006).

Herbal infusion is considered as a safe beverage to be consumed due to hardly detected or absence of heavy metals such as mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As) which affect our body health (Nookabkaew et al., 2006; Özcan et al., 2008). The allowable total amount of herbal infusion drinking is 1 L or three cups/day (100 mL per cup with 2 g of herbs), especially for those sensitive individuals including pregnant women. This is due to the presence of aluminum (Al) element in most of the herbal infusions like ginkgo, lemongrass, *A. vera*, jiaogulan, mulberry, and others, although only in tiny quantity. However, the accumulation of Al in the body can lead to organ toxicity when it exceeds the tolerable limits (Malik et al., 2013; Özcan et al., 2008; Nookabkaew et al., 2006).

In addition to mineral content, some organic acids are found in herbal infusions. Citric acid is an organic acid which plays an important role in retarding oxidative deterioration of lipids in foods while oxalic acid is a strong chelator for metal cations. Herbal infusion of Roman chamomile (*Chamaemelum nobile*) contained high organic acids including malic acid (3.06 g), followed by quinic (2.56 g), oxalic (1.99 g), and citric (1.46 g) acids (Guimarães et al., 2013).

Some specific carotenoids such as α-carotene, β-carotene, and β-cryptoxanthin are provitamin A. Calendula flower (*Calendula officinalis*) infusion (1.96 μg/mL) was found with the highest total carotenoids, followed by dandelion (*Taraxacum officinale*) infusion (0.718 μg/mL) and the lowest total carotenoids in violet leaves (*Viola odorata*) infusion (0.083 μg/mL) (Olsen et al., 2015). The authors reported a higher TCC was found in the raw and dried herb when compared to their respective infusions. This explains the important of solvent's polarity in extracting carotenoids from herbs.

From time to time, studies have shown that phytochemical compounds such as phenolic acids (Table 13.2), minerals, and organic acids are available in herbal infusions and these compounds have the beneficial effects in promoting good body health and reducing the risks of getting chronic diseases. In addition to the attractive flavors of herbal infusions, herbal infusions are getting more popular and easily accepted as daily beverages globally.

13.3 Beneficial Properties of Infused Water

13.3.1 Fruits

13.3.1.1 Antioxidant Effect

Fruits or vegetables are usually infused in water with their peels as peels are believed to have medicinal or nutritional potential and sometimes even more than the flesh. Xu et al. (2008) reported that hot water extract of citrus peels of Satsuma mandarin and Ponkan had almost the same antioxidant capacity as their respective methanol extracts. Among the hot water extracts, Ponkan showed a higher antioxidant capacity compared to Satsuma mandarin.

In Serbia, 26 types of commercially available drinks which included 11 fruit infusions, 13 herbal, black, and green teas were studied for their phenolic compounds and antioxidant properties. Fruit infusions such as cherry, strawberry, raspberry, forests fruits, apricot, sweet cherry, blueberry, apple, pomegranate, pineapple, and exotic fruits were analyzed. Fruit and tea infusions were prepared by adding 2 g of each type of samples to 200 mL of deionized water which

Table 13.2 Total Phenolic Content in Different Herbal Infusions

		Total Phenolic Content (mg GA/mL)					
Common Name	**Scientific Name**	**Atoui et al. (2005)**	**Vaquero et al. (2010)**	**Kaliora et al. (2014)**	**Sánchez-Burgos et al. (2013)**	**Ho et al. (2010)**	**Dalar and Konczak (2013)**
Greek mountain tea	*Sideritis syriaca*	0.37					
Mint	*Mentha piperita*	0.44	0.83				
Chamomile	*Matricaria recutita*	0.44					
Dictamnus	*Origanum dictamnus*	0.45					
Eucalyptus	*Eucalyptus globules*	0.47					
Sage	*Salvia fruticosa*	0.52		0.17		1.31	
Linden	*Tilia* sp.	0.77					
Black Ceylon tea	*Camellia sinensis*	3.53				2.72	
Chinese green tea	*Camellia sinensis*	5.07				2.50	
Yerba mate	*Ilex paraguaiensis*		0.93				
Lippia	*Lippia integrifolia*		0.92				
Oak leaves I	*Quercus resinosa*				6.91		
Oak leaves II	*Quercus grisea*				7.06		
Oak leaves III	*Quercus laeta*				5.75		
Oak leaves IV	*Quercus obtusata*				5.72		
Tolik	*Malva neglecta*						27.9
Giyamambel	*Plantago lanceolata*						80.4
Masicerk	*Verbascum cheiranthifolium*						60.6
Nérgiz	*Anchonium elichrysifolium*						28.1
Calba	*Phlomis armeniaca*						58.6
Baresa spi	*Salvia limbata*						56
Rosemary	*Rosmarinus officinalis*			0.04		0.78	
Cretan ditanny	*Origanum dictamnus*			0.42			
Thyme	*Thymus vulgaris*			0.29			
Marjoram	*Origanum majorana*			0.49			
St. John's wort	*Hypericum perforatum*			0.76			
Balm	*Melissa officinalis*					4.59	
Mint	*Mentha longifolia*					2.26	
Verbena	*Verbena officinalis*					1.97	
Lemongrass	*Cymbopogon citratus*					0.50	

had been heated to 95°C and allowed to steep for 10 min. Based on five antioxidant capacity measures scaled to relative percentages, antioxidant potency composite index (ACI) of fruit and tea infusions was determined. Cherry and raspberry exhibited the highest antioxidant power among all the fruit infusions and highest ACI compared to all the tea infusions. Cherry showed the TPC of 148.39 ± 0.11 g/kg and TFC of 29.95 ± 1.43 g/kg, whereas raspberry recorded TPC of 223.86 ± 0.27 g/kg and TFC of 31.65 ± 1.14 g/kg. Among all, the highest amount of (+)-catechin (1.47 ± 0.04 g/kg) was found in cherry infusion and the highest (−)-epigallo catechin gallate (1.96 ± 0.07 g/kg) was detected in strawberry infusion (Pavlović et al., 2013).

In addition, *Hyphaene thebaica* is a desert palm or also called as Doum or gingerbread palm. It is native to West India, sub-Saharan Africa, and Egypt. Both the fruit pulp and kernel are edible and also considered as faming food. Hot water infusion of the dried fruit pulp has been taken as a health tonic drink. Antioxidant property of dried fruit infusion was investigated and compared with Lipton® BT. Dried fruit powder and Lipton® BT leaves were put into individual glass bottle, containing boiling water and stirred continuous for 30 min. The extracts were filtered, evaporated at 35–40°C, and further freeze-dried. Then, it was redissolved in methanol. The results revealed that the antioxidant activity of doum fruit was comparable to BT. The activities expressed as mmol pure compound equivalent per g GAE content of extract were: (i) 2.85 mmol ascorbic acid equivalent (AAE) of hydrogen donating activity, (ii) 1.78 mmol ethylenediamine tetraacetic acid equivalent of Fe^{2+}-chelating activity, (iii) 192 mmol GAE of hydroxyl radical-scavenging activity, (iv) 3.36 mmol GAE inhibition of substrate site-specific hydroxyl radical formation, (v) 1.78 mmol GAE of superoxide radical-scavenging activity, and (vi) 3.93 mmol AAE of reducing power. Surprisingly, the iron chelation was about 14 times more potent (Hsu et al., 2006). Iron has been associated in the pathogenesis of particular central nervous system disorders, such as Alzhermer's, Parkinson's, and Huntington's diseases. The iron chelators can be utilized as therapeutic agents to treat or prevent these disorders (Richardson, 2004).

In another study, water infusion of leaves of *Rosaceae* family which includes strawberry, blackberry, and raspberry were examined for their antioxidant potentials against green and BT infusions, red, white wine, and fruit beverages. The leaves were ground and 1 g of it was let infused in 50 mL of boiled water for 20 min. Based on DPPH method, the antioxidant capacity of leave infusions was lower than red wines and tea infusions, yet comparable to the antioxidant capacities of fruit beverages and white wines. Furthermore, (+)-catechin, (−)-epicatechin, and procyanidin B1 were identified in raspberry leaves but all of these compounds in addition to epicatechingallate were found in blackberry leaves, whereas biologically active (+)-catechin, (−)-epicatechin, and EA were significantly contributed to the antioxidant capacity of the leaves infusions of all the plants examined in this study (Buricova et al., 2011).

A different study also conducted on blueberry leaves but studied on different cultivars such as one wild lowbush blueberry cultivar, six highbush blueberry cultivars, and one commercially obtained leaves. Among these, wild blueberry infusion had the largest TPC of 1879 mg/L GAE as well as ferric reducing/antioxidant power assay (FRAP) values of 20,050 μM. Overall, all 30-min infusions showed significant scavenging capability for radical of $ABTS^{\bullet +}$ and $DPPH^{\bullet}$ (Piljac-Žegarac et al., 2009). Moreover, water extract of *Vitex doniana* (black plum) was found to contain the highest DPPH radical scavenging inhibition and was significantly similar to vitamin C. In addition, the superoxide dismutase (SOD) and catalase (CAT) levels of the extracts were significantly higher in relative to the control. Besides, the extracts produced a significant decrease of liver malondialdehyde (MDA) compared to the control (Agbafor and Nwachukwu, 2011).

13.3.1.2 Detoxification

Natural compounds can be used as detoxifying agents as they can eliminate the toxic elements from human body by activating detoxification enzymes. This will provide protection from metabolic, genotoxic, and cytotoxic actions of environmental toxic agents (Saha and Das, 2003). *Punica granatum* Linn. (Punicaceae) which is also well known as pomegranate flower is consumed worldwide as a beverage, especially in Turkey. The plant infusion was prepared by immersing 2.5 g of dried flower leaves in 1 L of boiled water for 5 min. An animal model experiment was conducted to study the effect of the flower infusion on hepatopreventive and antioxidant potential. There were three experimental groups (control, trichloacetic acid (TCA), and TCA treated with the plant infusion) and each group consists of six Sprague-Dawley albino rats. TCA is a chemical carcinogen which can affect liver and other tissues of the body. The result depicted that there were increased level of hepatic damage indicating increased levels of markers such as aminotransferase and alanine aminotransferase enzymes in TCA-induced rats but the markers lessened in plant infusion-treated group. In addition, lactate hydrogenase and creatine kinase activities did not differ in TCA induced group but reduced in the plant infusion-treated group. Lipid peroxidation which may lead to many diseases also elevated significantly in the kidney, liver, brain as well as heart tissues of TCA exposed group whereas it was reduced in the plant infusion-treated group. With regard to antioxidant defense systems, glutathione *S*-transferase activity augmented significantly in the liver, spleen, and brain of the plant infusion-treated group while a significant reduction was detected in the kidney. Therefore, the researchers claimed that pomegranate leaves are able to activate phase II detoxifying agent and protect vital tissues against TCA caused damages. In conclusion, the plant beverage supplements such as water infusions may protect against oxidative stress and carcinogenic chemical induced liver injury and may be possibly used to prevent chronic degenerative liver diseases (Celik et al., 2009).

13.3.1.3 Energy Drink/Hydration

Fruits mainly consist of fructose and glucose. Unlike glucose which is readily used by all types of cell, fructose is specifically targeted to the liver where it is mainly converted into glucose and lactate. Ultimately, this will alter the hepatic function by raising glucose and lactate levels in the body. Herein, this may induce considerable effects on muscle metabolism which could lead to an improved performance during exercise (Rosset et al., 2017).

A study was conducted to prove that fruit infused water can be used to replace energy drink. A mixture of 138 g of apple, 118 g of banana, and 108 g of lemon may produce 212 kcal/L of energy and contains 61 g/L of carbohydrate which is equal to 6% of a carbohydrate beverage that is usually recommended as a sport drink. This mixture of fruits infusion was given to 24 young adults and they were divided into fasting only, fasting-water and fasting-fruit infused water groups. All subjects had to fast from 6 a.m. to 12 p.m. and blood glucose level was recorded for every 15 min. No significance difference was recorded at initial point but the glucose level in people taken fruits infusion water increased from the first 15 min and increased even higher at second 15 min. A drop of blood glucose level was recorded here after and beyond 60 min till the end of the study and there was no difference between the three experimental groups. Hence, the researchers claim that this fruit infused water can be utilized to retain blood glucose level and prevent hypoglycemic conditions (Ali et al., 2016).

13.3.1.4 Improve Lipid Profile

Ziziphus jujube fruit (ZJF) or red date is one of the medicinal plants that have been used widely and distributed to Europe, Australia, Southern, and Eastern Asia. These red dates contain alkaloids, glycosides, saponins, flavonoids, terpenoids, and phenolic compounds (Tripathi, 2014). In a clinical trial involving type 2 diabetic patients, ZJF infusion (10 g/100 mL boiling water) was given three times for 12 weeks. When compared to the control group without any treatment except for a balanced diet, the ZJF treated group showed changes in their lipid profile where the low-density lipoprotein (LDL) cholesterol, total cholesterol, and triglycerides were decreased significantly. In ZJF treated group, red dates also helps to alleviate blood glucose level by reducing the glycosylated hemoglobin (Yazdanpanah et al., 2017).

13.3.2 Vegetables

13.3.2.1 Antioxidant Effect

Ulcerative colitis and Crohn's disease are examples of inflammatory bowel diseases due to dysregulated immune response. Many alternative therapies are seek to sooth the signs and symptoms of this ailment such as *Aloysia triphylla* usage. About 40 g of crushed *Aloysia triphylla* or called as lemon verbena leaves were used to steep in 1 L of boiled water for 30 min and diluted to feed the rats. Some of these rats were induced colitis by using dextran sulfate sodium. Although the rats treated with infusion water did not reduce the inflammatory cells in the colon, they combat the oxidative stress in the colon by increasing the SOD and reducing lipid peroxidation (LPO) (Lenoir et al., 2011).

Among all the eight samples of Malaysian traditional vegetables namely *Anacardium occidentale* shoot, *Carica papaya* shoot, *Curcuma longa* leaves, *Etlingera elatior*, *Manihot esculenta* shoot, *Pithecellobium jiringa*, *Psophocarpus tetragonolobus*, and *Sauropus androgynous* tested by Huda-Faujan et al. (2015), the highest antioxidant activity was detected in water extracts of bunga kantan (*Etlingera elatior*) at 75.6%. Besides, the aqueous extract of *Sauropus androgynus* was found to demonstrate the best half maximal inhibitory concentration, IC_{50} value at 0.077 mg/mL. Many studies have postulated that antioxidant activities found in the Malaysian traditional vegetables such as *Cosmos caudatus* (Norhanom et al., 1999; Abas et al., 2006; Huda-Faujan et al., 2009), *Centella asiatica* (Norhanom et al., 1999; Huda-Faujan et al., 2009; Rahman et al., 2014), *Averrhoa bilimbi* (Nor Asna and Noriham, 2014; Rahman et al., 2014), *Morinda citrifolia* (Mohd Zin et al., 2002), *Melicope Lunu ankeda* (Othman et al., 2014), *Polygonum minus* (Norhanom et al., 1999; Huda-Faujan et al., 2009; Othman et al., 2014), and *Oenanthe javanica* (Norhanom et al., 1999; Huda-Faujan et al., 2009) were closely associated with their phenolic contents.

On the other hand, *Moringa oleifera* has been reported as a nutritious vegetable tree with variety of medicinal uses. Although *Moringa oleifera* is native to South Asia but it is also grown in Latin America and tropical Africa. It is known as a horseradish tree or drumstick tree. The leaves, immature pods, flowers, and fruits are all edible and have been used as daily food in India for 5000 years (Patel et al., 2010). Table 13.3 shows the pharmacological activities of different parts of *Moringa oleifera* infusion.

Table 13.3 Pharmacological Activities of Different Parts of *Moringa oleifera* Infusion

Parts of the Plant and Extraction Method	Method of Preparation	Pharmacological Activities	Mode of Study and Dosage
Leaves (Tahiliani and Kar, 2000)	Dried, ground, subjected to water extraction for 24 h at room temperature and vacuum dried	Alleviate hyperthyroidism Decreased hepatic lipid peroxidation	28 Male and female Swiss rats, 175 mg/kg body weight per day for 10 days
Leaves (Ghasi et al., 2000)	Ground and homogenized with distilled water	Hypocholesterolemic activity	15 Male Wistar rats, 200 mg/mL for 30 days
Leaves and flowers (Luqman et al., 2011)	Dried, subjected to water extraction, and vacuum dried	Antioxidant activity No toxicity of the extracts up to a dose of 100 mg/kg body weight	In vitro and 24 mice 0.01, 0.1, 1, 10, and 100 mg/kg body weight for 7 days

13.3.2.2 Laxative

Chenopodium album is also known as bathwa has been cultivated worldwide and consumed in India. Besides, infusion of the leaves is used as an enema for curing intestinal ulcers among Zulu tribes of Africa. It is claimed to have therapeutic effect in piles and diseases of eyes and throat. Infusion or decoction of these leaves possesses laxative, diuretics, anthelmintic, tonic, and aphrodisiac properties. It is prescribed for disease conditions such as hepatic disorders, biliousness, and splenic enlargement (Vohora et al., 1973).

13.3.2.3 Antihypertensive and Hypolipidemic Effects

Hibiscus sabdariffa Linn. (HS) is also known as roselle and thought to be native to Tropical Africa or Asia, India to Malaysia. The plant is around 3.5 m tall with alternate leaves, yellow flowers, red calyx, and red fruits after they mature and light brown kidney-shaped seeds. The red tea from the calyces is also called as Karkade. According to the Ayurvedic literature, the whole plant has medicinal values. The pharmacology evidences of this plant such as antioxidant, anti-hyperlipidemic, antihypertensive, hepatoprotective, anticancer, antipyretic, and many other activities so far have been documented (Mahadevan and Kamboj, 2009).

In a clinical trial, 60 diabetic patients suffering from mild hypertension were participated to study the effectiveness of sour tea (ST) or karkade from red calyces of HS against BT. The subjects were not in medications for either antihypertensive or hyperlipidemic condition.

The recruited patients were given infused drink of ST or BT two times a day for a month. Infusion was prepared by adding 240 mL of boiling water and 5 g of sugar to 2 g of dried plant and allowed to steep for 20–30 min. The average of systolic BP in ST consumed group was decreased significantly ($P < 0.001$) from 134.4 ± 11.8 to 112.7 ± 5.7 mmHg. In contrast, the average of systolic BP in BT consume group was increased significantly ($P = 0.002$) from 118.6 ± 14.9 to 127.3 ± 8.7 mmHg. The average pulse pressure also decreased significantly ($P < 0.001$) in ST consumed group from 52.2 ± 12.2 to 34.5 ± 9.3 mmHg whereas it showed increased significantly ($P = 0.01$) from 41.9 ± 11.7 to 47.3 ± 9.6 mmHg in BT consume group. There was no significant change reported on the diastolic BP of both groups. This study strongly suggested that consumption of ST tea may have antihypertensive effect on diabetic patients who have mild hypertension even with 5 g of sugar (Mozaffari-Khosravi et al., 2009a).

The effects of ST and BT were also studied for the hypolipidemic effect in diabetic patients. Sixty patients were involved in this randomized controlled clinical trial although only 53 patients concluded the study. The findings showed that ST elevated ($P = 0.002$) the high-density lipoprotein (HDL) cholesterol, also commonly known as good cholesterol whereas a significant ($P = 0.002$) decrease was observed in total cholesterol, LDL, and Apo-B100 triglyceride. Meanwhile, ST did not change the apolipoprotein A1 and lipoprotein (a) levels. As for BT group, the only significant change ($P = 0.002$) was observed in HDL cholesterol but showed an increase after the treatment. Thus, ST may also improve lipid profile of diabetic patients (Mozaffari-Khosravi et al., 2009b).

13.3.2.4 Antidiabetic Effect

There is a growing interest in alternative therapies especially for chronic diseases such as diabetes mellitus. Traditional phytotherapies have been used widely to prevent or manage this disease. In Nigeria, an ethnobotanical survey by means of semi-structured questionnaire of medicinal plants was conducted in five districts of Lagos state which is reputed for the diabetes treatment. Hundred respondents who are knowledgeable with 20–30 years of experience in traditional treatment of diabetes were interviewed. Surprisingly, the duration of treatments was usually between 12 and 16 weeks only and there were no known serious side effects reported in most of the cases. There were 50 medicinal plants being used so far and 20% of them were consumed in the form of infusions. It stated that *Vernonia amygdalina* Del. (VA) was the most consumed plant (32.6%) along with other medicinal plants. The leaves are served as stews or soups and considered to be a staple vegetable in equatorial Africa. Table 13.4 shows the water infusions of VA and other medicinal plants that were taken together as an antidiabetic phytotherapy in Lagos, Nigeria (Gbolade, 2009).

Table 13.4 Water Infusions of VA and Other Medicinal Plants That Were Consumed as an Antidiabetic Phytotherapy in Lagos, Nigeria

Mixture of Plants	Dosage of Prescriptions
VA leaves alone should be squeezed with water	Drunk twice daily
VA and *Ocimum gratissimum* leaves are squeezed with water	Not stated
VA, *Peperomia pellucida* and *Ocimum gratissimum* leaves are squeezed with water and filtered	Three glass cups daily
VA and *Ocimum gratissimum* leaves and stem and bark of *Bridelia micrantha* are squeezed with water	Not stated
VA and *Ocimum gratissimum l*eaves are squeezed with water	Not stated
VA leaves and *Bidens pilosa* fruits are soaked in water	One glass cup three times daily

On the other hand, *Momordica charantia*, known as bitter gourd or bitter melon is also claimed to possess hypoglycemic effect. It is widely consumed by diabetic patients to control their glucose level. Commercial tea preparations of *Momordica charantia* leaf and fruit are commercially available for this purpose in Philippines. An in vivo study involving 126 male normoglycemic albino mice was performed to analyze the hypoglycemic activity of this plant. *Momordica charantia* fruit tea weighing 1.75 g and leaf tea weighing 2.00 g were steeped in 175 and 200 mL hot water, respectively, for 10 min and vigorously stirred. The doses administered to mice were based on the weight of tea/kg birth weight (BW) of mice as follows: 200 mg/kg, 100 mg/kg (subjected to light stirring only), and 50 mg/kg of BW. The mentioned treatments were given to the mice 30 min after administration of 5 g of glucose/kg BW as a part of oral glucose tolerant test (OGTT) followed by measurement of blood glucose within a 3 h period at 30 min intervals. *Momordica charantia* fruit tea significantly ($P = 0.001$) lowered blood glucose during 0.5–1.0 h. The highest activity was recorded in 100 mg of fruit tea/kg BW during 0.5 h and it was even comparable with the positive control, glimepiride solosa. The blood glucose lowering effect was also sustained for 2.5 h. Meanwhile, *Momordica charantia* leaf infusion had significantly reduced the blood glucose level of OGTT across 3 h. Charantin was reported to be responsible for the blood glucose-reducing capacity of the seed and fruit of the plant. Thus, *Momordica charantia* can be used to control blood glucose level although further investigation is needed to support the findings (Ragasa et al., 2011).

13.3.3 Herbs

13.3.3.1 Antioxidative Effect

Oxidative stress occurs when reactive oxygen species (ROS) are generated by free radicals. This phenomenon causes damage to human body's cellular and extracellular macromolecules which subsequently leads to tissue injury. Thus, formation of free radical is also a major leading cause of aging and some degenerative disorders such as cancer, cardiovascular disease, and cataract. They also cause declination of the immune system and dysfunction of the brain (Atoui et al., 2005; Apak et al., 2006).

Atoui et al. (2005) studied on the antioxidant activity of green, BT, dictamnus, sage infusions with DPPH free radical scavenging method, and the activities was reported in QE and trolox equivalents (TE). The green tea was found to exhibit highest hydrogen donating capacity (0.38 QE; 0.57 TE), followed by BT (0.34 QE; 0.54 TE), dictamnus (*Origanum dictamnus*) (0.25 QE; 0.4 TE), and sage infusions (*Salvia fruticosa*) (0.18 QE; 0.27 TE). In another study, herbal infusion of St. John's Wort (*Hypericum perforatum*) (430.8 TE; 66.5 AAE) demonstrated the highest antioxidant activity which was determined using DPPH (in TE) and FRAP (in AAE), followed by marjoram (*Origanum majorana*) (149.6 TE; 18.9 AAE) and Cretan ditanny (*Origanum dictamnus*) (141.7 TE; 17.8 AAE) while the lowest activity was found for rosemary infusion (*Rosmarinus officinalis*) (7.7 TE; 0.52 AAE) (Kaliora et al., 2014). In addition, Apak et al. (2006) studied the antioxidant activity of scarlet pimpernel (*Anagallis arvensis*), sweet basil (*Ocimum basilicum*), and lemon balm (*Melissa officinalis*) using ABTS and CUPRAC. The strongest antioxidant activity was observed for scarlet pimpernel (CUPRAC 1.63 mmol TR/g; ABTS 1.02 mmol TR/g), followed by sweet basil (CUPRAC 1.18 mmol TR/g; ABTS 0.77 mmol TR/g) and lemon balm (CUPRAC 0.99 mmol TR/g; ABTS 0.63 mmol TR/g). Ascorbic acid, a crucial antioxidant vitamin was also found in scarlet pimpernel, sweet basil, and lemon balm at a concentration of 340, 260, and 210 mg, respectively, when infused in 150 mL of water. These also suggested that herbal infusion is able to provide a satisfactory source of antioxidants in diets (Apak et al., 2006).

All the above-mentioned antioxidant activities of herbal infusion were greatly attributed by their total phenolic compounds. A significant positive correlation ($P < 0.01$) was demonstrated between antiradical activity with phenolic content of *p*-OH-benzoic acid, protocatechui acid, GA, chlorogenic acid, epicatechin, catechin, kaempherol, and QE, respectively (Kaliora et al., 2014). Strong positive correlations between antioxidant capacity and TPC were also shown by herbal infusions (Apak et al., 2006; Atoui et al., 2005; Dalar and Konczak, 2013). This could be due to the capability of some phenolic contents in quenching LPO, preventing DNA oxidative damage, scavenging the ROS/nitrogen species or suppressing the ROS formation through inhibiting the enzyme activity, and chelating trace metals. Therefore, consumption of herbal infusions as beverages has gained increasing public interest due to their high antioxidant content (Apak et al., 2006; Atoui et al., 2005; Vaquero et al., 2010; Dalar and Konczak, 2013; Kaliora et al., 2014).

Moreover, a synergistic effect was observed when flavoring substance such as lemon, bergamot, clove, or cinnamon was added into the herbal infusions. The ability of the samples to donate hydrogen was determined using DPPH radical scavenging activity where a lower EC_{50} was found with higher antioxidant activity due to lower amount of samples required to decrease the initial DPPH concentration. BTs with lemon, bergamot, clove, grounded cinnamon, or stick cinnamon demonstrated significant antioxidant activities ($P < 0.005$) with the lower EC_{50} of 0.54, 0.48, 0.52, 0.53, and 0.52, respectively, when compared to BT alone (control; 0.68). Among the BTs with different flavoring substances, the highest antioxidant activity was found in BT with bergamot (Büyükbalci and El, 2008). This suggests that preparation of herbal infusions together with some flavored plants might enhance the antioxidant properties rather than the individual action of the herbs.

However, the antioxidant capacity of dried powdered herbs showed considerable losses when storage period up to 15 months by testing the stability of antioxidant activity with SOD mimetic activity, LPO inhibitory capacity and total thiol content. Results showed a 7.4-fold decrease of SOD mimetic activity and a significant declined of LPO inhibitory capacity ($P < 0.001$) for herbal infusions prepared from 15 months stored powdered herbs compared to the fresh powdered herbs. Meanwhile, the total thiol (–SH) content was also declined from 0.55–1.71 to 0.12–0.21 mg/g in those herbal infusions prepared from 15 months stored powdered herbs. Thus, this implicates the storage time of grounded herbs used in preparation of infusion is crucial with the concern of their beneficial effects without a declination of the antioxidant capacity (Naithani et al., 2006).

13.3.3.2 Antimicrobial Effect

Recently, bacterial resistance to antimicrobial drugs such as antibiotics, antifungals, antivirals, antimalarials, and antihelmintics has emerged as a serious threat to global public health. Through the previous studies, herbal infusion can serve as an additional method to prevent infection from some microbes due to their potential antimicrobial effect.

Vaquero et al. (2010) showed that herbal infusions of Yerba mate (*Ilex paraguaiensis*), lippia (*Lippia integrifolia*), mint (*Mentha piperita*), and burrito (*Wendtia calysina*) reduced ($P < 0.05$) the viable cells of *Escherichia coli* significantly in 1.5, 1.02, 1.05, and 1.09 log cycles, respectively. However, the clarified infusions from the respective herbs with removal of phenolic compounds were found to exhibit lower effectiveness in reducing the viable cells count of *E. coli*. This shows that the antibacterial effect of herbal infusion might be due to the presence of phenolic compounds.

In addition to *E. coli*, Sánchez-Burgos et al. (2013) reported that herbal infusion of oak leaves from four different species (*Q. resinosa, Q. laeta, Q. grisea, and Q. obtusata*) demonstrated different degrees of antimicrobial activity. *Q. resinosa* showed an inhibitory effect against *Staphylococuss epidermidis* with the inhibitory halo of 7.56 ± 2.14 mm and minimum inhibitory concentration (MIC) at 0.348 mg/mL. Inhibitory effects toward *Klebsiella pneumonia*, the pathogen that lead to pneumonia and bronchitis were seen when treated with *Q. grisea* (14.94 ± 1.70 mm; MIC 0.886 mg/mL), *Q. resinosa* (14.56 ± 0.22 mm; MIC 0.547 mg/mL), *Q. obtusata* (8.72 ± 0.11 mm; MIC 0.84 mg/mL), and *Q. laeta* (8.04 ± 0.21 mm; MIC 1.3 mg/mL). *Q. resinosa* showed the best antimicrobial effect against the other three species, with the inhibitory effect against Gram negative bacteria of *Proteus mirabilis* that leads to kidney stones (16.94 ± 0.90 mm; MIC 0.708 mg/mL); *Proteus vulgaris* that leads to bacteremia and sepsis (16.35 ± 1.32 mm; MIC 0.265 mg/mL); and *Enterobacter aerogenes* that leads to various infections (11.6 mm; MIC 0.534 mg/mL). Other than the inhibitory effect on bacteria, *Q. resinosa and Q. grisea* also showed an inhibition on yeast, *Candida albicans* with inhibitory halos of 6.66 and 9.61 mm while the MIC of 0.5 and 1.78 mg/mL, respectively (Sánchez-Burgos et al., 2013).

Moreover, Oh et al. (2013) demonstrated the bactericidal effect of Yerba mate (*Ilex paraguariensis*) against Gram positive bacteria with the MIC of 5.83, 5.42, and 6.88 mg/mL against oral pathogens (*Streptococcus mutans* and *Streptococcus sobrinus*) and food-borne pathogen (*Listeria monocyogenes*), respectively. The mechanism of action of this bactericidal activity was contributed by nerolidol found in the Yerba mate infusion. In addition, herbal infusion from the rosemary's leaves (*Rosemarinus officinalis*) which contained myricetin also demonstrated antimicrobial activity against two oral pathogens, *Streptococcus mutan* and *Streptococcus sobrinus*. However, Gram negative bacteria were found to be more resistant compared to the Gram positive bacteria due to their lipopolysaccharide outer membrane. This outer membrane prevents the diffusion of hydrophobic compounds including some phenolic compounds. With the antimicrobial activity of herbs against some oral pathogens, drinking of those herbal infusions might assist in eliminating cariogenic bacteria from oral cavity and maintaining dental health (Oh et al., 2013).

In addition, *Sesbania grandiflora*, *Telosma minor*, and *Senna siamea* are flowers that are popularly used in Thailand for its health benefit in curing those patients with stomach disorder. The effect of this aqueous extract on microbial inhibition for three types of bacteria, namely *Bacillus cereus*, *E. coli*, and *Staphylococcus aureus* was investigated by Krasaekoopt and Kongkarnchanatip (2005). In this water extraction, ratio of flower to water used was 1:2. Continuous shaking condition for 7 days was applied for this extraction. The results showed that all of these flower aqueous extractions for 7 days exhibited high antimicrobial properties against all bacteria, particularly the highest inhibition zone that can be observed on *Staphylococcus aureus.* Moreover, *Senna siamea* and *Sesbania grandiflora* extracts possessed higher antimicrobial activities than *Telosma minor* extract.

Other than pathogenic bacteria, herbal infusion was found with antimalarial effect in getting rid of malaria. This antimalarial effect was attributed by the active compound of artemisinin which has capability in reducing the survival of parasites in red blood cells by cleaving the heme and iron (II) oxide. Artemisinin was found in herbal infusions of annual worm wood (*Artemisia annua L.*) with the concentration of 0.54, 0.61, and 0.64 mg/mL when having the infusion time of 1, 24, and 48 h, respectively. Meanwhile, a higher concentration of artemisinin was found in water extraction compared to the organic solvents such as acetonitrile and hexane. This could be due to the use of water with medium polarity which has a better dissolving capacity for artemisinin and better extraction efficiency of the main phenolic constituents of annual worm wood such as chlorogenic acids. The presence of chlorogenic acid would provide a synergistic effect in giving better antimalarial effect (Carbonara et al., 2012).

13.3.3.3 Anti-inflammatory Effect

Cytokines such as interleukin 8 (IL-8) can be pro-inflammatory and play the crucial role in angiogenesis, providing microenvironment for tumor progression and neutrophil chemotaxis. Kaliora et al. (2014) reported that herbal infusions were found to decrease the production of pro-inflammatory cytokine IL-8 significantly ($P < 0.05$) in the HT 29 colon cancer cells, with the best efficacy found in sage (*Salvia officinalis*) infusion followed by cretan dittany (*Origanum dictamnus*), thyme (*Thymus vulgaris*), marjoram (*Origanum dictamnus*), St. John's wort (*Hypericum perforatum*), and the lowest efficacy in rosemary (*Rosmarinus officinalis*) infusion. In addition, a decrease in the production of IL-8 was observed in the PC3 prostate cancer cells treated with the same herbal infusions, with the efficacy order from thyme to sage, cretan dittany, marjoram, rosemary, and St. John's wort (Kaliora et al., 2014). Similar findings were also found in the study of Kogiannou et al. (2013) where herbal infusions of pink savory (*Satureja thymbra*), oregano (*Origanum vulgare*), mountain tea (*Sideritis syriaca*), pennyroyal (*Mentha pulegium*), and chamomile (*Matricaria chamomilla*) decreased IL-8 levels significantly ($P < 0.05$) in both HT 29 colon and PC3 prostate cancer cells (Kogiannou et al., 2013).

However, the exact mechanisms of the herbal infusions in preventing inflammation or reducing the cytokines production were not clearly reported, except sage and chamomile. Ehrnhöfer-Ressler et al. (2013) demonstrated that the presence of volatile compounds of 1,8-cineole, borneol, camphor, and α-/β-thujone in herbal infusion of sage were able to reduce the release of pro-inflammatory ILs IL-6 and IL-8 significantly ($P < 0.05$) in the human gingival fibroblast (HGF-1), with a mean inhibition of 50%–76%. Reduction of IL-6 and IL-8 is important in modulating the host defenses against periodontal bacteria (Ehrnhöfer-Ressler et al., 2013). Meanwhile, chamomile was found to contain high amount of genistein which could reduce IL-8 production by inhibiting the NF-κβ signaling pathway (Kogiannou et al., 2013).

Evidences from in vitro and in vivo experiments conducted by Sadeghi et al. (2012) showed that herbal infusions were able to improve immune response in animal model. Replacement of drinking water with herbal infusions of cinnamon (*Cinnamomum verum*), thyme (*Thymus vulgaris*), and turmeric (*Curcuma longa*) on broiler chickens for 21 days demonstrated improved antibody titers against newcastle disease virus. A better improvement in the immune response was observed for the broilers with cinnamon infusion compared to the thyme or turmeric infusion (Sadeghi et al., 2012).

13.3.3.4 Antihyperglycemic Effect

Acanthaceae (*Strobilanthes crispus*) with the common name of “pokok pecah beling” is a native plant to Madagascar, Indonesia, and Malaysia. Its leaves are commonly used in preparation of infusion to prevent diabetes and have diuretic, antilytic, and laxative effects. Fadzelly et al. (2006) studied the in vivo antihyperglycemic effect of acanthaceae infusion on 42 hyperglycemic Sprague-Dawley rats with six rats per group. A significant ($P < 0.05$) decreased in blood glucose level was observed in rats fed with acanthaceae infusion for 21 days compared to the group with diabetic drug (glibenclamide). Reduction of blood glucose level was achieved by the mechanism of action of the active compound of a flavonoid, epicatechin. This flavonoid is able to restore and regenerate β-cells of Langerhans’ islet in the pancreas.

In addition, the postprandial blood glucose level is always being a concern for diabetic patients. One of the controlling ways to prevent increasing in the glucose level is through inhibiting body enzymes, α-glucosidase or α-amylase that involve in releasing glucose from foods. Alpha-glucosidase is an enzyme that hydrolyzes starch and disaccharide to glucose while α-amylase breaks down large polysaccharide to glucose. Thus, hydrolysis of dietary carbohydrates could be retarded in the presence of α-glucosidase and α-amylase inhibitors, which subsequently helps in suppressing postprandial hyperglycemia. Herbal infusions have been reported to exert α-amylase and α-glucosidase inhibition activities at different levels and the same study also reported that the more effective way in controlling postprandial hyperglycemia with the minimum side effects was those herbal infusions calba (*Prunus armeniaca*), Baresa spi (*Stagmomantis limbata*), and giyamambel (*Plantago lanceolata*) with a low α-amylase inhibitory activity but showed a high α-glucosidase inhibitory activity. This is because concurrently inhibition of both enzymes may lead to abnormal bacterial fermentation in colon due to the presence of undigested carbohydrates (Dalar and Konczak, 2013).

13.3.3.5 Anti-glycation Effect

Other than diabetic, diabetic's complications are also one of the major public concerns. One of the common complications is microvascular resulted by deposition of advanced glycation end products (AGEs). AGEs can be resulted from the early and late-stage glycation of amino group. AGEs can be deposited in collagen, the extracellular matrix protein which alters physio-chemical properties and physiological function. This triggers the nuclear factor-κβ signaling pathway to induce inflammation and result in cell damage. AGEs are involved in the pathogenesis of microvascular complication in both diabetic and aging individuals. Herbal infusion was found with AGEs inhibitors and exhibited anti-glycation capacity based on the phenolic content especially the flavonoid content. Study showed that the strongest anti-glycation capacity was found in balm (89.8%), followed by mint (47.8%), BT (38%), sage (33.4%), common verbena (30.4%), rosemary (18.8%), and lemongrass (3.0%). Thus, herbal infusion could also serve as an alternative healthy beverage to prevent diabetic and aging microvascular complications (Ho et al., 2010).

13.3.3.6 Body Weight Control

Obesity has been reported as the risk factor for some chronic diseases such as cardiovascular disease and diabetic disorder. Obesity is always resulted by absorption of fatty acids by body, the simplest form of fat due to hydrolysis of lipid to fatty acids by lipase, an enzyme that produced from pancreas. Suppression of pancreatic lipase has been reported to control obesity and body weight from herbal infusions; and the suppression effect is dose and phenolic compounds dependent. Giyamambel (*Plantago lanceolata*), masicerk (*Verbascum cheiranthitolium*), and Baresa spi (*Stagmomantis limbata*) exhibited strong suppression on pancreatic lipase with high levels of phenolic compounds (Dalar and Konczak, 2013). Herbal infusions of acanthaceae (*Strobilanthes crispus*) reduced total cholesterol level of six *Sprague dawley* rats at day 7- and 21-treatment as well as the LDL. It is contributed by the plant sterol, β-sitosterol, and stigmasterol in the leaves of acanthaceae that inhibit cholesterol absorption in intestine (Fadzelly et al., 2006).

13.3.3.7 Antihypertensive Effect

Angiotensin converting enzyme (ACE) is found in catalyzing angiotensin I to angiotensin II, leading to an elevation of BP with the occurrence of hypertension. Thus, inhibitory of ACE activity is reported as a prevention of hypertension. Dalar and Konczak (2013) reported that Baresa spi (*Stagmomantis limbata*) and Tolik (*Malva neglecta*) showed an ACE inhibitory activity up to 35% and 34%, respectively. However, the authors found that the inhibitory was not correlated with their antioxidant capacity (Dalar and Konczak, 2013).

In a clinical trial, 65 pre- and mildly hypertensive adults without antihypertensive medications were treated with hibiscus infusion (*Hibiscus sabdariffa*) for 6 weeks. At the end of treatment, BP and mean arterial pressure were lowered with more significant reduction in systolic BP compared to the placebo ($P < 0.001$). The mechanisms of action of hibiscus infusion in lowering BP were due to the effects of anthocyanins which act on calcium channels in dilating the vessel as vasorelaxant and inhibiting the activity of ACEs in converting angiotensin I to II (McKay et al., 2010).

13.3.3.8 Chemopreventive Effect

Herbal infusions have also been reported to possess chemopreventive effect. Cretan dittany (*Origanum dictamnus*) demonstrated a remarkable growth suppression reaching 95% in human colorectal adenocarcinoma cell line (HT29) and approximately 80% after 24 h and 90% after 48 h in human prostate cancer cell line (PC3). Guimarães et al. (2013) proved that Roman chamomile (*Chamaemelum nobile*) was able to inhibit the growth of five human tumor cell lines (breast carcinoma cell line, MCF-7; non-small cell lung cancer cell line, NCI-H460; colon carcinoma cell line, HCT-15; cervical carcinoma cell line, HeLa; and hepatocellular carcinoma cell line, HepG2) (Guimarães et al., 2013).

Antitumor effect found in herbal infusions was suggested to be attributed by the presence of phenolic content and other phytochemicals. Cretan dittany with high amount of carvacrol and rosmarinic acid was believed to have the ability to exhibit antiproliferative effect (Kaliora et al., 2014). Furthermore, Roman chamomile was found to have high content of phenolic compounds including flavonoids (flavonols and flavones), phenolic acids, and derivatives such as caffeorlyquinic acid, glucuronide, and so on. These abundant of phenolic compounds were proven to have the capabilities in regulating cell proliferation and death pathways including cell growth, inhibition of kinase activity, induction of apoptosis, and suppression of matrix metalloproteinases secretion (Guimarães et al., 2013).

Two herbal infusions, pink savory and oregano exhibited antiproliferative effects on cancer due to their high content of phenolic acids (thymol) and hydroxycinnamic acids (caffeic acid, ursolic acid, and carvacrol), respectively. Caffeic acid is able to inhibit lipoperoxidation, induce cell cycle arrest and apoptosis, inhibit signal transduction pathway, and inhibit nitrosation as well as nitration. On the other hand, thymol and carvacrol can lead to cancer cell death by reacting with cancer cells' membrane lipids and mitochondria, causing cell membrane to become more permeable and resulting in cell components leakage (Kogiannou et al., 2013). QE is also mainly found in mountain tea and inhibits tumor growth by reducing expression of Ras protein, the protein that involved in cell growth, differentiation, and survival. Thus, through reduction of Ras protein, expression of epidermal growth factor receptor and tyrosine kinase activity could be inhibited which subsequently inhibit the proliferation of cancer cells (Ranelletti et al., 2000).

In overall, all the beneficial properties and its mechanism of actions of herbal infusions are summarized in Table 13.5.

Table 13.5 Beneficial Properties and Its Mechanism of Actions of Herbal Infusions

	Beneficial Properties	Mechanism of Actions
Herbal infusions	Antioxidant capability	**(i)** Quenching lipid peroxidation **(ii)** Preventing DNA oxidative damage **(iii)** Scavenging ROS/RNS **(iv)** Suppression ROS formation
	Antimicrobial effects	Inhibitory effects toward *S. epidermidis, K. pneumonia, P.vulgaris, P.mirabilis, E. aerogenus,* etc.
	Anti-inflammatory	Inhibition of cytokine production
	Anti-hyperglycemic	Inhibition of body enzymes, α-glucosidase or α-amylase, in releasing glucose from food
	Anti-glycation	Inhibition of AGEs production
	Body weight control	Suppression of pancreatic lipase
	Anti-hypertensive	Inhibition of ACE activity
	Chemopreventive	Regulation of proliferation and cell death pathways by: **(i)** inhibition of kinase activity **(ii)** induction of apoptosis **(iii)** suppression of matrix metalloproteinases secretion
	Anti-malarial	Active compound of artemisinin in reducing the risk of resistance of the protozoa

13.4 Conclusion

The natural plant infused water consists of high nutritional value and health beneficial properties which make it as a preferred healthy drink among world population, especially those health conscious consumers. Various studies reported that infusions of phytochemicals from fruit, vegetable, or herb into water possess potential therapeutic benefits that can provide benefits to mankind. The phytochemicals from the plant sources have also been widely exploited by industries to be used as supplements, food additives, food enhancer, and ingredients for making perfumes.

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14

MAIN MICROBIOLOGICAL POLLUTANTS OF BOTTLED WATERS AND BEVERAGES

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14.1 Introduction

Water is essential for every form of life, being necessary for all biological processes. At the global level, water is a limited resource, fact which requires care in its use for a sustainable preservation of water resources. Clean, safe, and hygienic water are other aspects that people take care for assuring public health. The consumption of water of inadequate quality could lead to high rates of waterborne disease. The quality of tap water is not always the best, reason for which in the last years, consumption of bottled water has increased. But although people perceive the bottled water being clean and safe, this is not always the truth, the bottled water being also chemically or microbiologically contaminated, raising risks for diseases (Khaniki et al., 2010).

Because the isolation of pathogenic microorganisms from the water involves a complex and costly analysis as well as the fact that their presence in water is not always constant, in practice an indirect method of highlighting their potential presence is used, involving the determination of some microbiological indicator species, whose presence in water signals the risk of fecal pollution and implicitly the risk of contamination with pathogenic microorganisms. In general, the following indicator parameters are used to determine the degree of microbiological contamination of water: total number of microorganisms grow at 22°C; total number of microorganisms grow at 37°C; total coliform bacteria (total coliforms), fecal coliforms; the presence of *Escherichia coli*; fecal streptococci (enterococci).

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In special situations (new water sources, control of water treatment plants, accidental pollution, water epidemics, etc.) the following parameters are also determined: the presence of sulfate reducing *Clostridium* species and the presence of *Clostridium perfringens*; the presence of *Pseudomonas aeruginosa*; the presence *Salmonella* species; enteric bacteriophages (Chifiriuc et al., 2016). It was proved that none of these established tests is absolute, because sample of water although consistent with these requirements could be at the origin of some infectious diseases. For example, samples negative for *E. coli* indicator can be contaminated with viruses or protozoa like *Cryptosporidium* spp. (Edberg et al., 2000).

14.2 Main Microbiological Pollutants of Bottled Waters

Drinking water contaminants can be classified in physical, chemical, biological, or radiological substances or matter. Some of these contaminants may be harmful for the animal and human organisms, while others may be harmless. Biological contaminants are represented by bacteria, protozoa, yeast, fungus, and toxins produced by these organisms as well as viruses that are responsible of different diseases in humans, most frequently gastroenteritis (Table 14.1).

Table 14.1 The Major Types of Microbiological and Viral Contaminants of Water and the Associated Diseases

Type of Contaminant	Species	Type of Infection
Bacteria	*Campylobacter jejuni, Campylobacter coli*	Mild self-limiting gastrointestinal illness
	Escherichia coli	Gastrointestinal illness and kidney failure
	Helicobacter pylori	Capable of colonizing human gut that can cause ulcers and cancer
	Legionella pneumophila	Lung diseases when inhaled
	Mycobacterium spp.	Lung infection in those with underlying lung disease, and disseminated infection in the severely immunocompromised persons
	Shigella sonnei	Mild self-limiting gastrointestinal illness and bloody diarrhea

Table 14.1 The Major Types of Microbiological and Viral Contaminants of Water and the Associated Diseases—cont'd

Type of Contaminant	Species	Type of Infection
	Salmonella enterica	Mild self-limiting gastrointestinal illness
	Vibrio cholera	Gastrointestinal illness, watery diarrhea
	Pseudomonas aeruginosa	Hospital-acquired infections
	Klebsiella pneumoniae	Pneumonia, typically in the form of bronchopneumonia
	Aeromonas hydrophila	Gastroenteritis, septicemia, traumatic and aquatic wound infections, and infections after medical leech therapy
	Enterobacter cloacae	Gastrointestinal illness
Viruses	Adenovirus	Respiratory illness and occasionally gastrointestinal illness
	Astrovirus	Gastroenteritis in children
	Caliciviruses (rotaviruses, noroviruses)	Mild self-limiting gastrointestinal illness
	Enterovirus (polioviruses, coxsackie viruses, echoviruses)	Mild respiratory illness
	Hepatitis A and E viruses	Liver disease and jaundice
Protozoans	*Cryptosporidium* spp.	Enteric disease
	Giargia lamblia	Intestinal disease, diarrhea among children
	Naegleria fowleri	Primary amebic meningoencephalitis
Yeasts and fungi	*Penicilium* spp., *Penicillium citrinum, P. glabrum*	
	Aspergillus spp.	
	Candida spp., *Candida glabrata*, and *Candida albicans*	
	Cladosporium spp., *Cladosporium cladosporioides*	
	Alternaria alternate	
	Rhizopus spp.	
	Fusarium spp.	
	Trichoderma viride	
	Aspergillus spp.	
	Phoma spp.	
	Phialophora richardsiae	
Toxins	Geosmin (*Chaetomium globosum*)	
	Aflatoxins (*Aspergillus* spp.)	
	Patulin (*Aspergillus* spp., *Penicillium* spp., *Byssochlamys* spp.)	
	Zearalenone (*Fusarium* spp.)	
	Fumonisins (*Fusarium* spp.)	
	Neosolaniol (*Fusarium* spp.)	
	Ochratoxin (*Aspergillus* spp., *Penicillium* spp.)	

14.2.1 Main Bacterial Contaminants

Coliform bacteria in bottled water represent a great threat to public health, especially for infants, young children, and immunocompromised persons that could contact waterborne diseases, even at lower infectious doses. World Health Organization (WHO) recommends that potable water should have below 20 CFU/mL heterotrophic bacterial counts with no coliform bacteria, fecal coliforms, *E. coli*, enterococci, and *P. aeruginosa* (Khatoon and Pirzada, 2010). Coliform bacteria belong to *Enterobacteriaceae* family and include species of the following genera: *Citrobacter*, *Enterobacter*, *Escherichia*, *Hafnia*, *Klebsiella*, *Serratia*, and *Yersinia*. The presence of coliform microorganisms in drinking water represents a sign of fecal contamination and indicates the potential contamination also with pathogenic bacterial species such as *Shigella* spp., *Salmonella* spp., or *Vibrio cholerae*. They are used traditionally as indicators of water quality because the testing methodology is simple and inexpensive.

E. coli can survive in drinking water at 15–18°C for 4–12 weeks and does not multiply significant in the external environment. According to WHO (2006) *E. coli* are rarely found in water in the absence of fecal pollution, and no differentiation is made between pathogenic and nonpathogenic *E. coli* when this species is isolated from water. Therefore, water that contains *E. coli* is unsafe for consumption due to the strong association between *E. coli* and fecal contamination.

At least six different main groups of *E. coli* were differentiated, based on the specific virulence factors of the strains and the clinical features of the disease, from which enterotoxigenic (ETEC), enterohemorrhagic (EHEC), and enteroinvasive (EIEC) serotypes are most harmful and could be transmitted by contaminated water (Bettelheim, 2003; Scheutz and Strockbine, 2005).

ETEC serotype can cause infantile gastroenteritis. Intense watery diarrhea that lasts several days, dehydration and malnutrition in young children represents some of the manifestation of the disease. Although in developed countries the number of the cases is small, in the developing country, because of an adequate clean water and poor sanitation, the reports indicate that this serotype is an important cause of diarrhea, being the most frequently isolated bacterial enteric pathogen in children under 5 years of age. This serotype is also known as the main common cause of “travelers’ diarrhea” at people from developed countries who travel in these developing regions.

EHEC serotype produces Shiga-like toxins and determines abdominal pain, bloody diarrhea, and hemolytic uremic syndrome. The symptoms last 7–10 days, but in some cases, infections result in acute renal failure. Although EHEC strains are not ordinarily contaminants of treated drinking water, some reports indicate that some drinking water sources contaminated with human sewage or cattle feces. Some authors reported that EHEC strains could survive some months in manure and water-trough sediments, isolated from different sources of water such as ponds or streams, wells, and water troughs.

EIEC strains determine gastroenteritis, enterocolitis, and dysentery accompanied by well-known symptoms as abdominal cramps, diarrhea, emesis, febrility, chills, a generalized malaise, and stools with blood and mucus. Similar with *Shigella*, they are invasive species that can enter and multiply in the intestinal epithelial cells of the distal large bowel in humans (Cabral, 2010).

Campylobacter spp. infections together with *Salmonella* spp. and *Shigella* spp. infections are the leading cause of acute gastroenteritis worldwide (Frost, 2001). The main sources of contamination with *Campylobacter* spp. are consumption of raw meat, untreated drinking water, raw milk, and the presence of pets (Brown et al., 2004; Friedman et al., 2004). Also, the most common species isolated in developed and developing countries are *Campylobacter jejuni* and *Campylobacter coli*. Their presence in water is due to wastewater discharge and farming activities (Evans et al., 2003). Survival of *Campylobacter* in different type of waters (ground, surface, and drinking waters) is conditioned by a variety of factors such as temperature, nutrients, water microbiota, and biotic interactions (Talibart et al., 2000; Cools et al., 2003). A study by Tatchou-Nyamsi-König et al. (2007) whose objective was to evaluate *C. jejuni* survival of at 4°C and 25°C in filtered natural mineral water proved that the microaerophilic *C. jejuni* survive better at temperature around 4°C, high temperatures (16–22°C) affecting the cell viability. The study also demonstrated that even in the presence of biodegradable organic matter the bacteria could survive and multiply for a relatively long time, despite of the presence of oxygen, especially at low temperature (Tatchou-Nyamsi-König et al., 2007).

Other contaminants of bottled water could be represented by *Enterococcus* species that are Gram-positive cocci facultative anaerobes displaying alkaline and salt tolerance. Genus *Enterococcus* formerly referred to as the fecal streptococci or Lancefield group D comprises many species of which *Enterococcus faecalis* and *Enterococcus faecium* are predominant. Most enterococci do not multiply in water but can survive in water longer than coliforms and most enteric pathogens. The 2006 WHO drinking water report showed that enterococci are indicators of chronic fecal pollution serving as a marker for fecal pathogens that survive longer in water than *E. coli* (WHO, 2006). Water containing enterococci should be considered unsafe due to the strong association between enterococci and fecal contamination (Report of the Scientific Committee of the Food Safety Authority of Ireland, 2009).

Pseudomonads found in soils, ground water, marine environments, plants, are part of the normal microbiota of bottled water. *P. aeruginosa* is Gram-negative opportunistic bacteria which are responsible of a wide range of infections especially in patients with compromised host defense mechanisms (Zamberlan da Silva et al., 2008). The presence of *P. aeruginosa* causes urinary and respiratory tract infections, in patients who are severely immunocompromised (e.g., patients with neutropaenia, cystic fibrosis, and severe burns), being difficult to eradicate due to its high intrinsic resistance and ability to transfer its resistance genes. *P. aeruginosa* requires a high oral infectious dose, of minimum 1.5 million bacteria to cause an infection and normally *P. aeruginosa* does not infect the healthy tissue. *P. aeruginosa* cannot grow and survive in natural mineral water, and when detected, it is in low numbers (Leclerc and Moreau, 2002). Edberg et al. (1996) conducted a study in which they determined the numbers and types of bacteria found in three water sources (bottled water, water cooler water, and tap water). They took samples from a wide variety of water types and determined the presence of heterotrophic plate count (HPC) bacteria, total coliforms, and *P. aeruginosa*. They also determined the virulence factors expression, susceptibility to antibiotics, acid lability, and cytotoxicity testing using Hep-2 cells. Their results showed that all water sources presented a normal bacterial content, and only 2% of bottled water samples were positive for *P. aeruginosa*.

Vantarakis et al. (2006) investigated the microbiological quality of over 1000 samples of bottled non-carbonated ("still") mineral water, from more producing companies in Greece, during the period 1995–2003. Around 14% of the samples were inadequate according to Greek water regulation. The genera identified from the samples were *Pseudomonas*, *Aeromonas*, *Pasteurella*, *Citrobacter*, *Flavobacterium*, *Providencia*, and *Enterococcus*, the species *P. aeruginosa* being the most frequently isolated.

Another study from Puerto Rico identified as main bacterial contaminants from commercial bottled waters species *as Pseudomonas fluorescens*, *Corynebacterium* sp. *J-K*, *S. paucimobilis*, *Pseudomonas vesicularis*, *Aeromonas baumannii*, *Pseudomonas chlororaphis*, *Flavobacterium indologenes*, *Aeromonas faecalis*, and *Pseudomonas cepacia* (Reyes et al., 2008).

Helicobacter (H.) pylori is a Gram-negative, microaerophilic bacterium involved in the development of gastric adenocarcinoma, gastritis, and mucosa-associated lymphoid tissue lymphoma. Furthermore, *H. pylori* are the primary cause of ulcers in the stomach and duodenum. More than 50% of world populations have been infected with *H. pylori*, but exact routes of transmission are still unknown, contaminated water playing an important role in spreading of *H. pylori* to humans (Ranjbar et al., 2016).

Legionella pneumophila is an aerobic, pleomorphic, flagellated, nonspore-forming, and Gram-negative bacterium. In a study that used 68 commercial bottled mineral waters were identified *Legionella* antigen in eight samples (confirmed by PCR as *L. pneumophila*), but were negative in cultures. Whether the bacteria are alive or dead the risk for infection is high especially for the immunocompromised patients (Klont et al., 2006).

Mycobacterium (M.) tuberculosis is a pathogenic bacteria from *Mycobacteriaceae* family. *M. tuberculosis* is part of a complex that contains at least nine species: *M. tuberculosis* sensu stricto, *M. africanum*, *M. canetti*, *M. bovis*, *M. caprae*, *M. microti*, *M. pinnipedii*, *M. mungi*, and *M. orygis*. Until 1882 *M. tuberculosis* was the only clinically significant species, then numerous reports led to the discovery of atypical nontuberculous mycobacteria (NTM). NTM can survive, persist, and develop in drinking water supply systems. Recent data disclose that water may be the transporter for these mycobacteria that infect or colonize the host. NTM species can cause opportunistic infections in immunocompromised patients. In AIDS the major mycobacteria species and the most common cause of death is *Mycobacterium avium*. In an US study focusing on *M. avium* and *M. intracellulare in drinking water showed that these mycobacteria can be clinically relevant in human population. From 139 cisterns, noncarbonated bottled waters, or reservoir samples, 46 (33%) were positive for NTM. The most frequently NTM species isolated from water are: M. kansasii, M. mucogenicum*, and *M. peregrinum (Covert* et al., 1999*)*.

14.2.2 Viruses

More than 140 enteric viruses can infect humans and are considered to be emerging waterborne pathogens because of their high stability in the environment and resistance to current water treatment processes. HEntVs include families: (i) *Picornaviridae* (polioviruses, enteroviruses, coxsackieviruses, echoviruses, and hepatitis A virus), (ii) *Caliciviridae* (noroviruses and sapoviruses), (iii) *Astroviridae* (astroviruses), (iv) *Reoviridae* (rotaviruses), (v) *Hepeviridae* (hepatitis E virus), and (vi) *Adenoviridae* (adenoviruses) (Fong and Lipp, 2005). These viruses are associated with mild respiratory illness, gastroenteritis, but also encephalitis, meningitis, myocarditis (enteroviruses), cancer (polyomavirus), and hepatitis (hepatitis A and E viruses). Other viruses such as polyomaviruses and cytomegalovirus influenza and coronaviruses can potentially be spread through water but evidence is not clear (WHO, 2011). Viral infections are in the most cases self-limiting in healthy individuals, but can cause higher rates of morbidity in children under the 5 years old, in elderly, immunocompromised people, and pregnant women. In developing countries, waterborne virus-based diseases present higher level because widespread malnutrition and numerous HIV-positive people (Gall et al., 2015).

Contamination of drinking water is supported by (i) low infectious doses of viruses; (ii) persistence long periods of time in water; and (iii) very high numbers of viral particles in feces. Also, drinking water can transports viruses through inhalation (e.g., showering) or by direct contact with eyes or skin (e.g., swimming). The United States Environmental Protection Agency (USEPA) is assessing adenovirus, enteroviruses, caliciviruses, and hepatitis A virus for potential regulatory action (U.S. EPA, 2009). The current regulations involve the removal or inactivation of 99.99% of enteric viruses using approved techniques. Viruses are small particles and conventional treatment, including filtration is usually ineffective, so the most viruses are inactivated using oxidants. Water treatment techniques include physically removing viruses through conventional treatment and inactivating viruses using ultraviolet light or chemical substances such as chloramines, chlorine dioxide, chlorine, and ozone.

The presence of viruses is not usually on the list of the main indicators for microbiologic contamination in bottled water, because detection of viruses from drinking water is more difficult in comparison to detection of bacteria. Viral multiplication requires the use of tissue culture, involving time, expertise, labor, and expensive equipment. Furthermore, some of these viruses are difficult (e.g., adenovirus serotypes 40 and 41) or impossible (human norovirus, hepatitis A virus) to cultivate in cell cultures. Molecular biology techniques such as ELISA and PCR allow a rapid analysis of viruses, but they do not distinguish between particles with infectious properties versus particles with non-infectious properties.

It has been estimated that 30%–90% of waterborne disease outbreaks worldwide are caused by human *enteric viruses* (HEntVs). HEntVs are transmitted primarily by the fecal-oral path, either direct from person-to-person or via ingestion of contaminated food or water.

The human adenovirus (HAdV) belongs to the *Adenoviridae* family and can be a potential marker of human fecal contamination in water. Enteric viruses are more resistant to environmental conditions and water treatment by chlorination and filtration than enteropathogenic bacteria. In water there is no potential for replication because the viruses are obligate intracellular parasites, but however, the viral degradation is slower than that of bacteria in water and the amount of remaining viruses has a significant potential for starting an outbreak (Nascimento et al., 2015).

Choi and Jiang (2005) showed that 16% of the river samples in California, United States were positive for HAdV. Also, Albinana-Gimenez et al. (2009) found the HAdV in river water samples in Barcelona. Furthermore, Dong et al. (2010) detected the HadV in sewage and recreational water samples from New Zealand. Wyn-Jones et al. (2011) showed that European recreational and fresh water samples were positive for HadV (60.6%). In China, Ye et al. (2012) described 100% the presence of HAdV in river and drinking water samples.

Both *hepatitis A and E* are reported worldwide. Hepatitis A (HEA) is particularly frequent in countries with poor sanitary and hygienic conditions (in Africa, Asia, and Central and South America). Countries with economies in transition and some regions of industrialized countries where sanitary conditions are under-standard and are also highly affected (southern and eastern Europe and some parts of the Middle East). In recent years, some outbreaks have occurred in areas of conflict and emergencies, such as war zones, and in sites for refugees.

An estimated 20 million infections and 3.3 million symptomatic cases of hepatitis E (HEV) occur annually worldwide with a number of deaths estimated at 56,000. Cases and outbreaks of this disease often go undiagnosed or misdiagnose, confused with other forms of hepatitis because of the similarity of this disease with other forms of acute viral hepatitis, and limited availability and use of specific diagnose tests for it. The incubation period of hepatitis E varies from 2 to 10 weeks, with most cases occurring 4–6 weeks after exposure. Hepatitis E virus has a 7.2-kb single-stranded RNA genome that forms 27–34 nm non-enveloped virions. The virus has at least four distinct genotypes, 1 and 2 infect only humans, and are responsible for the majority of human diseases caused by infection with this virus, and genotypes 3 and 4 are found among mammalian animals, including pigs, wild boar, deer, and only occasionally infect humans. Genotypes 1 and 2 have been associated with large waterborne outbreaks, and genotype 3 has been identified in occasional small foodborne outbreaks reported from developed countries. Heating to 60°C for a few minutes has been shown to inactivate a large proportion of HEV particles suggesting that drinking water can be rendered safe by pasteurization or boiling. Several epidemics of hepatitis E have been found to be related to the failure of chlorination, suggesting that chlorine treatment protects against hepatitis E. Thus, although there is no direct evidence that chlorine inactivates HEV, chlorination of drinking water with adequate residual chlorine levels at the point of consumption continues to be a good public health intervention (De Serres et al., 1999).

Norovirus epidemics associated with drinking water are reduced in developed countries, although it was implicated in a waterborne outbreak in Spain. More than 4000 cases of gastroenteritis were detected during April 11–25, 2016, the patients presenting symptoms such as vomiting, diarrhea, nausea, abdominal pain, or fever. The epidemiologic investigation revealed a correlation between the outbreak and drinking bottled spring water from office water coolers. The contaminated samples fulfilled all the other requirements for natural mineral water. The company producing these waters recalled anyway more than 6000 containers of suspected water as a safety measure (Albert et al., 2017).

14.2.3 Protozoan Drinking Water Contaminants

Water is also an important vehicle of many parasitic diseases. *Cryptosporidium*, an emerging pathogen, is a major cause of enteric infections in humans and animals. Cryptosporidiosis can be severe especially in children, elderly people, and malnourished persons and life-threatening in those whose immune systems is depressed. In AIDS patients, infections with *Cryptosporidium* are lethal, no drug therapy has been found to be effective (Fayer et al., 2000). The oocysts are transmitted either directly, by host-to-host contact or indirectly, by drinking contaminated water or consumption of contaminated food (Franco and Neto, 2002).

Recent data showed that cysts are resistant in 100% chlorine for 48 h. The shell of the cyst is disintegrated by the intestinal content of animals and humans. Therefore, elimination of cysts from water can be done by filtration.

In water, *Cryptosporidium* is found in a cyst form, protected by a shell making it resistant to traditional disinfectants. In the intestinal tract, the cyst walls are destroyed, releasing the parasite that multiply into the body and provoke symptoms such as cramps, diarrhea, or even death. In 1993 in Wisconsin over 400,000 persons suffered from gastrointestinal illness when a contamination with *Cryptosporidium* was found in the public water supply, and over 100 immunocompromised people died. More recently in other cities such as New York City, Nevada, Oregon, and Georgia was reported the presence of *Cryptosporidium* in water. Specialists estimate that ~50% of the city water supplies may have *Cryptosporidium* present but most cities have not yet been tested.

Giardia lamblia is a flagellated protozoan that causes significant intestinal diseases in both humans and animals. Epidemiological features of *Giardia* are similar with *Cryptosporidium*, representing one of the major public health concerns regarding water utilities today. *Giardia* is a reemerging infectious agent due to high number of outbreaks of diarrhea among children (Thompson, 2000). In Brazil the level of contamination of ground and raw water with *Cryptosporidium* and *Giardia* is very high, and also bottled mineral water was tested. *Giardia* cysts can be eliminated from water by a filtration method using filters that retain all particles of at least 4 µm. In Mexico, three brands of mineral water, the protozoan was found using membrane filtration and in vitro culture tests (Nichols et al., 2004).

Other protozoa species identified in water samples are the nonpathogenic amoebae *Vahlkampfia vahlkampfia*, *Naegleria gruberi*, and *Acanthamoeba astronyxis* and the flagellate *Bodomorpha minima*. In France, a nonpathogenic amoebic species was detected in mineral waters originating from small-capacity regional plants. Franco and Neto detected 13 *Cryptosporidium* oocysts by membrane filtration followed by immunofluorescence in 2 of 13 bottled water samples.

Naegleria is another ameba commonly found in warm freshwater (lakes, rivers, and hot springs) and soil. The ameba can be found also in swimming pools that are poorly maintained, minimally chlorinated, and/or unchlorinated, in water heaters because *Naegleria fowleri* grows best at temperatures up to 115°F (46°C) and also in salt water, like the ocean (CDC). Only one species of *Naegleria*, that is, *Naegleria fowleri* infects people. The incidence of infection with *Naegleria fowleri* is very low, only 40 cases being reported in the United States in the 10 years from 2007 to 2016. The majority of infections have been caused by *Naegleria fowleri* from freshwater located in southern-tier states.

14.2.4 Yeasts and Fungi

Candida (*C.*) spp. are the most prevalent yeasts isolates from the water samples. There are now at least 17 species of *Candida* with medical importance, some of them being found in water samples: *C. parapsilosis*, *C. glabrata*, *C. albicans*, *C. tropicalis*, and *C. guilliermondii*. The incidence of nosocomial infections caused by *Candida* strains is growing due to changes of the implicated species, antibiotic resistance, and host-related predisposing factors. Some studies reported the presence of fungal biofilms in municipal water distribution systems. Fungi established in biofilms in water systems are more resistant to water treatment, and can colonize filters in treatment plants, and consequently affect the water treatment. The ecology of fungi in biofilms has been studied only to a small degree, and further research should aim to investigate the features of fungi grown in biofilms (Gunhild et al., 2009).

In the literature, few reports are regarding the occurrence of yeasts and fungi in treated and bottled mineral waters (Yamaguchi et al., 2007).

From filamentous fungi, *Penicillium (P.)* spp., *Penicillium citrinum*, *Penicillium glabrum, Cladosporium cladosporioides*, *Alternaria alternate*, *Cladosporium, Rhizopus, Aspergillus*, and *Phoma* were the most frequently isolated species. Some of these are potentially pathogenic, allergenic, and toxigenic species.

Cabral and Pinto (2002) reported the presence of filamentous fungi in more the 100 samples of still bottled mineral water produce by different commercial brands (eight) from Argentina.

In a study in 2001 *Aspergillus fumigatus* was found in tap water from Rikshospitalet University Hospital in Oslo. *Aspergillus fumigatus* is a fungal pathogen causing infections at immunocompromised patients, suggesting that hospital water systems may serve as a transmission path for fungal infections. These data indicate that hospital water may contain also other species of fungi, including potential pathogens. A hypothesis is that fungi in water are aerosolized into air when water passes the system, such as taps and showers, reaching to immunocompromised patients. Air levels of *Fusarium* and *Aspergillus* were found to increase in hospital environments after running showers multiple times.

When it comes to the allergenic potential of fungi in water, three cases have been reported from Sweden and Finland. An outbreak with *Phialophora richardsiae* in water was reported. Two case reports from Finland indicated fungal contaminated water as the source of hypersensitivity pneumonitis. *Trichoderma viride* was the most dominant species in Norwegian drinking water and has been associated with asthma in children living in water-damaged homes.

14.2.5 Main Microbial Toxins Found in Water

The allergic potential of fungi in drinking water is not fully documented, large epidemiological studies being needed to investigate the presence of different toxins. Several microorganisms can cause taste and odor problems in drinking water. Several fungal species, such as, for example, *Chaetomium globosum* have been found to produce geosmin, a compound related with earthy odor and taste in drinking water. In addition, fungi may produce a variety of other compounds with distinctive off-flavors and tastes.

Mycotoxins are secondary metabolites produced by some fungi species. Exposure of humans or animals to them can cause serious health problems, some of them are considered carcinogenic. Such exposure is likely to occur from dietary intake of contaminated food, water, or beverages. Therefore, actions to prevent mycotoxin contamination of water have began in water treatment plants, consisting in first filtering the water and finally add adequate disinfectants to remove or mitigate fungi or their toxic metabolites Several of the species of *Penicillium* and *Aspergillus* are known to produce mycotoxins in other substrates, such as food and beverages. Some fungi, including *Penicillium* spp., *Aspergillus* spp., *Fusarium* spp., and *Claviceps* spp. are known to produce mycotoxins such as patulin, aflatoxins, and zearalenone. Toxins such as: aflatoxins, ochratoxin, fumonisins, and neosolaniol were identified by LC-MS/MS (Al-Gabr et al., 2014; Ribeiro et al., 2006).

Cyanobacteria (*Anabaena*, *Microcystis*, *Clyndospermosis nodularis*) produce water blooms that increase the level of toxins. They can act as hepatotoxins and neurotoxins, and can kill animals (goats, sheep, horses, pigs, dogs) within minutes or hours of water ingestion from these lakes. Toxins produced by cyanobacteria may also have mutagenic effects. Annually these toxins produce 100,000–200,000 of serious illnesses with neurological sequelae/10,000–20,000 deaths.

Algae also synthesize biotoxins, causing frequent intoxications by ingestion (diarrhea, neurotoxic phenomena) in tropical/subtropical areas, generating serious neurological sequelae (amnesia, paralysis). Microcystin is 1000 times more toxic than cyanide. Annually, 10,000–50,000 cases/year of ciguatera toxin poisoning are reported. Algal toxins are relatively stable in the dark and can last for at least 1 week in water (Chifiriuc et al., 2016).

14.3 Main Microbial Contaminants of Beverages

The contamination of microbial beverages occurs during fabrication process. Microbial problems of the beverages can be separated in two categories: (i) the spoilage of the product due to the growth of the microorganism in the juice that causes its deterioration, making it unpleasant for human consumption; and (ii) the contamination of the product due to the growth of microorganism determines food poisoning. The raw materials but also the environment conditions are the risk factors.

Soft drinks are high in water activity and often rich in vitamins and minerals, so they represent a good growth medium for different microorganisms. On the other hand due to the acidity of the medium, a few microorganisms can survive and multiply. Aciduric microorganisms are the main contaminants of the bottled beverages: yeasts, bacteria, molds, and mycotoxins (Table 14.2).

14.3.1 Yeasts

Yeasts are the main microbial contaminants of beverages, due to their capacity to survive in an acidic environment and at high carbonation levels. These species have an optimal pH value at 3.0–6.5, but are able to survive from pH 1.5–8.5. *Zygosaccharomyces bailii*, *Saccharomyces*, *Brettanomyces*, *Hanseniaspora*, *Hansenula*, and *Pichia* are the most encountered species founded in beverages involved in spoilage (Lawlor et al., 2009; Sperber, 2009). The process of spoilage could have many aspects: (i) the beverages become

Table 14.2 The Main Microbial Contaminants of Beverages

Type of Contaminant	Species	Type of Contamination
Yeasts	*Zygosaccharomyces bailii* *Saccharomyces* *Brettanomyces* *Hanseniaspora* *Hansenula* *Candida davenportii* *Candida parapsilosis* *Pichia* *Debaryomyces* spp. *Rhodotorula* *Sporidiobolus* *Sporobolomyces* *Aureobasidium*	Beverage spoilage
Molds	*Aspergillus* *Penicillium* *Rhizopus* *Cladosporium* *Alternaria* *Fusarium* *Byssochlamys spectabilis* *Talaromyces* spp. *Penicillium arenicola* *Neosartorya* spp.	Beverage spoilage
Bacteria	Lactic acid bacteria (LAB) *Lactobacillus (L.) paracasei, L. brevis, L. buchneri, L. plantarum, L. perolens, Leuconostoc mesenteroides, Weissella confuse* spp. Acetic acid bacteria (AAB)- (*Acetobacter, Gluconobacter, Gluconacetobacter*) Coliforms (*Klebsiella, Citrobacter, Enterobacter*) Spore forming bacteria (*Propionibacterium cyclohexanicum, Clostridium butyricum, Clostridium sporogenes, Alicyclobacillus* sp.)	Beverage spoilage
Toxins	Aflatoxins, ochratoxin A, patulin, trichothecenes and zearalenone	Beverage spoilage
Pathogenic species	Bacteria (*Salmonella, Yersinia enterocolitica, Listeria monocytogenes, E. coli*) Viruses (Hepatitis A, norovirus, and rotavirus) Protozoa (*Cryptosporidium parvum*)	Foodborne disease

inappropriate for a nonalcoholic drink due to the accumulation of high level of ethanol (as end product of yeasts fermentation) (Stratford, 2006), (ii) some yeasts species degrade preservatives from the beverages, changing the pH of the product, and further the flavor (Stratford et al., 2007.). Species as *Candida davenportii*, *Candida parapsilosis*, or *Debaryomyces* spp. could induce spoilage of the product when the production process goes wrong. The presence of the red aerobic yeasts *Rhodotorula*, *Sporidiobolus*, and *Sporobolomyces* and the black genus *Aureobasidium* indicates a bad hygiene, but usually not determine the spoilage of the beverages (Davenport, 2005).

14.3.2 Molds

Molds can survive also in the conditions found in beverages (pH values), but unlike yeasts, molds are strict aerobic species and require oxygen for growth. Spores of *Aspergillus, Penicillium, Rhizopus, Cladosporium,* and *Fusarium* can survive in beverages and could often be detected in soft drinks. They produce pectinases that change the taste and flavor of the product, toxic compounds and allergens. The most involved mycotoxins in spoilage of beverages are aflatoxins, ochratoxin A, patulin, produced by *Aspergillus, Penicillium, Fusarium, or Alternaria* and trichothecenes and zearalenone produced by *Fusarium* species (Juvonen et al., 2011; Scholte et al., 2004; Swanson, 2011). Heat-resistant molds as *Byssochlamys spectabilis*, *Talaromyces* spp., *Penicillium arenicola,* and *Neosartorya* spp. survive at 90°C (sterilization-pasteurization) determine spoilage of pasteurized juice.

14.3.3 Bacteria

Lactic acid bacteria (LAB) are the main bacterial species involved in beverage spoilage: *Lactobacillus paracasei*, *L. brevis*, *L. buchneri*, *L. plantarum*, *L. perolens*, and also *Leuconostoc mesenteroides*, and *Weissella confusa* (Back, 2005). Their metabolism products determine loss of carbonation, an increasing astringency in soft drinks, modification of smell (Lawlor et al., 2009). Another category of bacteria found in beverages are acetic acid bacteria (AAB)—a group of acid-tolerant bacteria that grow at pH 3.0–3.8 and produce some acids (acetic, gluconic, lactic, and succinic acids). Their growth determines flavor changes, package swelling, ropiness, haze, or sediments, especially in case of beverages packaged in PET bottles (oxygen-permeable containers). Coliforms, although acid intolerant species, are able to multiply in beverages with low pH values and produce extracellular polymers being detected in biofilm in plant environments (Kregiel and Rygala, 2010). *Propionibacterium cyclohexanicum*, a

Gram-positive pleomorphic rod, survives in pasteurized beverages. *C. butyricum, Clostridium sporogenes*, and *Alicyclobacillus* sp. are other spore-forming bacterial species, succeeding to survive and often associated with the spoilage of soft drinks (Kregiel, 2015).

14.3.4 Pathogenic Species

Besides above-mentioned microbial species involved in spoilage of beverages, there were also identified some pathogen species that do not belong to autochthonous microbiota of the fruits. The contamination has fecal origin and the contaminants could survive for different periods of time in juice. The most isolated species from beverage-related outbreaks of foodborne diseases are the EHEC pathotype of *E. coli*, the serotype O157:H7, and various serotypes of *Salmonella*, species that are able to survive up to 48 h in cola drinks (Parish, 2009; Sheth et al., 1988). Other species, as *Yersinia enterocolitica* and *Listeria monocytogenes* survive long periods in different juice concentrates maintained in the freezer and in freshly orange juice (pH 6.3) and moreover, incubated at a low temperature (4°C) usually enhances their survival (Lucero Estrada et al., 2010; Degirmenci et al., 2012). Protozoa and viruses require a host cell for replication, but can survive long time in the environment, as oocysts, for example, and can also be associated with fruit juice-related disease outbreaks. *Cryptosporidium parvum* was isolated from juice and cider. Hepatitis A, norovirus, and rotavirus could potentially transmit diseases via improperly produced beverages (Kregiel, 2015).

14.4 Conclusion

In the past years, the consumption of bottled water and soft drinks is preferred to consumption of tap water, the public considering them to be sterile, uncontaminated due to the fact that these products are more processed, and somehow more controlled. But, the risk for health should not be minimized, taking into account the microbial metabolic diversity and versatility, making different species capable to survive, and even multiply in the conditions offered by bottled waters and beverages. On the other hand, the supplementary procedural steps (packaging, bottling, handling, transport) may sometimes increase the risk of microbial contamination of the final product. Therefore, the consumption of bottled waters and beverages is not free of any risks regarding microbial contamination and consequent water or foodborne disease, especially in countries where the legislation and control of these products are not strictly regulated and respected.

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15

ENERGY USE AND ENERGY SAVING POTENTIALS IN FOOD PROCESSING AND PACKAGING: CASE STUDY OF NIGERIAN INDUSTRIES

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15.1 Introduction

Energy as a basic need for different purposes in industrial facilities, its huge amount is needed for countries with faster economic growth. Energy serves as a crucial factor for economic growth, competitiveness, and employment of any country. It is consumed in the industrial sector by a diverse group of industries including manufacturing, agriculture, mining, and construction (Abdelaziz et al., 2011). The objective of an efficient energy market is to provide energy commodities to power the industrial, transport, household, and service sectors of the economy. Hence, energy remains the lubricant of sustainable economic growth.

Energy use in the industrial sector depends majorly on the level of technology used, the industries concentration, the capacity utilization, and the level of maintenance practice. Energy is consumed in the industrial sector for a wide range of activities, such as processing and assembly, space conditioning, and lighting. In aggregate, the industrial sector uses more energy than any other end-use sector, consuming about one-half of the world's total delivered energy (Oyedepo et al., 2015).

The industrial sector uses a great portion of energy resources, much of which is wasted due to variety of inefficiencies and poor practices. More efficient use of energy is recognized as a key factor for sustainable development. In view of this fact, it becomes increasingly important to assess major causes of deficiency and energy degradation mechanisms to be able to develop systematic approaches for

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designing more sustainable energy systems (Sayyed et al., 2012). The need to conserve energy in manufacturing industry is of paramount importance, thus making the cost of energy of immediate interest to Managers and Engineers in this sector. In order to reduce the operating and maintenance costs to a minimum, the cost of energy consumption, which is the prime factor under operating cost, must be closely monitored (Aiyedun et al., 2008).

According to He et al. (2011), energy saving is an important task today and in the future. The implementation of energy-saving policies can promote the structural adjustment of industries and products and affect the enhancement of energy efficiency in production and processing. The analyses of consumption patterns and the assessment of feasible energy conservation possibilities show that the potential for energy conservation in the industrial sector and in all sectors is substantial (Yang and Mingguang, 2011).

Energy performance of machines and plant directly associated with the production process is a function of efficiency of energy utilization in a manufacturing industry. Hence, it is important to account for total consumption, cost, and how energy is used for each commodity such as steam, water, air, and natural gas. It is the responsibility of energy manager to focus his professional attention on how to reduce energy consumption per unit of production, that is, energy efficiency.

Energy management and related energy savings in industry sector are well-known issues as various legislative acts and standards have been adopted in recent years (Noro and Lazzarin, 2016). For example, in Italy, Directive 2006/32/EC on energy end-use efficiency and energy services adopted in Italy by D. Lgs. n. 115/08; in Kenya, Energy Act 2006 and Energy (Energy Management) Regulations 2012 govern and regulate the Energy Efficiency and Conservation activities (Oimeke, 2013); in Japan, the Energy Conservation Act was enacted in 1979 and has subsequently been revised several times. It has contributing to the sound development of Japan's economy by setting up necessary measures for the rational use of energy by factories, buildings, transport, and machinery and equipment (Shiel et al., 2011); in Russia, the Federal law on energy conservation and energy efficiency (# 261-FZ), which was adopted on 23 November 2009, aims to reduce the intensity of electricity, heat, water, and gas consumption in order to help Russia approach European consumption levels by 2020 (http://www.energosovet.ru/npb1189.html).

Understanding the benefits of high industrial productivity as a veritable tool to industrialization, successive governments in the country since independence have adopted various polices, schemes, and incentives toward realization of this all important objective. Some of these policies include the import substitution/indigenization policy (1972), the Structural Adjustment Programme (SAP) of (1986), the

Bank of Industry and Small and Medium Equity Investment Scheme (2000), the Electricity Power Sector Reform Act (EPSRA) of (2005), and the National Integrated Industrial Development (NIID) blue print (2007) (Ugwoke et al., 2016).

Despite these policies, available statistics indicate that the industrial sector in Nigeria is experiencing slow growth and one of the factors responsible for this to a considerable extent is the poor energy consumption. The survey by the Manufacturing Association of Nigeria (MAN) carried out in the first quarter of 2006 painted a gloomy picture of the crisis in the Nigerian industrial sector. According to the survey, only 10% of manufacturing concerns in Nigeria could operate at 48.8% of installed capacity, 60% of the companies operating were barely able to cover their average variable costs while 30% had to completely shut down due to inadequate supply of electricity (Ogunjiobi, 2015).

In Nigeria's industrial sector, energy-efficiency policy is almost completely absent and far behind developed countries. The government did implement some measures, namely first, an energy audit and preparation of an "energy passport," and second, the adoption of a national energy management standard on the basis of international standard ISO 50001. However, current Nigerian legislation does not compel companies to implement energy management systems. In addition, the lack of long-term financial funding for small- and medium-sized enterprises and the lack of an energy services market also do not stimulate industrial companies to increase energy efficiency.

In the food processing industry, a substantial amount of energy is consumed. Excessive use of energy is usually associated with many industrial plants worldwide, and food processing plants are no exception. Enormous potential exists for cost-effective improvement in existing energy-using equipment. Hence, a thorough assessment and analysis on how energy is consumed in food processing industry is important as it investigates the possibility of potential energy saving in the industry. Factors responsible for the consumption of energy are the activity, structure, and efficiency changes. Understanding these factors will give insight into whether energy is used efficiently and the possibility of its saving (Olanrewaju et al., 2015). Also, application of good housekeeping measures could result in appreciable savings in energy. Therefore, it is imperative to introduce and disseminate information about modern energy-saving technologies in the food processing industry which is focused on this chapter.

According to Mossie (2016), replacing failed electric motors with energy-efficient or premium-efficient electric motors; scheduled and proper greasing of electric motor bearings, reducing electric motor system friction losses, properly sizing electric motors to the load; testing questionable equipment before and after repair, improving the fuel consumption efficiency, improving lighting systems; and other measures that can be immediately implemented or implementation plan after energy losses assessment are very important steps to improve over all energy efficiency in food processing industries.

Several researchers have explored the energy use and energy-saving potentials in food processing industry in the last few years. Results show readily achievable, cost-effective, reduction in industrial consumption through effective energy management practices and energy-efficient equipment. Aderemi et al. (2009) assessed electrical energy use efficiency in selected Nigeria food industries. The study examined various patterns of energy consumption and the sources of energy wastage in the industries. From the study, the following were identified major sources that led to electrical energy waste and in-efficient energy utilization in the industries: energy loss as a result of worn out or slack/misaligned belts, power factor of electrical equipment, among others.

Aiyedun et al. (2008) investigated the energy efficiency in Nigerian Eagle Flour Mills Limited, Ibadan. The results showed that energy was not quite efficiently utilized as the energy productivity increased substantially from $0.369\,\mathrm{MJ\,kg^{-1}}$ in 1996 to $0.716\,\mathrm{MJ\,kg^{-1}}$ in 2000. In their study, Noah et al. (2012), a comprehensive energy audit of Vitamalt Nigeria Plc, Agbara was carried out to assess the pattern of energy consumption and possibilities of saving energy in the plant. The results of the study revealed that significant savings and improvement in energy usage is achievable.

Olanrewaju et al. (2015) assessed possible energy potential in a food and beverage industry by application of IDA-ANN-DEA approach. The integrated model applied to the selected food and beverage industry revealed that approximately 11% of energy consumed could be saved. Adedeji and Badmus (2012) carried out energy, exergy, and economic analyses of energy sourcing pattern in a Nigerian brewery. The result showed that diesel fuel combustion, whether for local electricity generation via internal combustion engines or for process steam raising in boilers, has adversely affected the efficiencies of energy utilization in the company. Energy audit of selected food processing industry and distillation and bottling in Nigeria was carried out by Oyedepo and Aremu (2013). From the study, electrical motors were observed to be the major consumer of electric energy accounting for 40%–47% of total electrical energy used in the selected industries. It was also observed that none of these companies under review utilized their energy effectively as they all have their energy used ratio far below 1.

Energy utilization and carbon dioxide emission during the production of fresh, peeled, diced, and juiced tomatoes were assessed by Karakaya and Özilgen (2011). Result showed that transportation appears to be the highest energy consumer and the most important source of CO_2 emission in the tomato-processing industries. The energy consumption and the CO_2 emission associated with production and application of the chemical fertilizers are among the stages where environment friendly progress seems to be possible. The authors concluded that by providing information to the consumers about the energy cost and CO_2 emission associated with each product may convince the producers to use cleaner energy sources. Energy use patterns in tomato paste production in Integrated Farms Limited, Dadin-kowa, Gombe State, Nigeria was assessed by Abubakar et al. (2010). Inefficient energy utilization was identified in the following: use of aging electric motors and malfunctioning of other auxiliary equipment and general wastage.

Goyal et al. (2014) identified thermal energy, mechanical energy, electrical energy, and human energy as energy patterns used in rice-milling industries. The major energy consuming equipment in the rice-milling units are: boilers and steam distribution, blowers, pumps, conveyers, elevators, motors, transmission systems, weighing, etc. Based on the investigation of this study, wide variety of technologies has been evolved for efficient use of energy for various equipment of rice mills, so far, only few have improved their energy-efficiency levels. As most of the rice mills use old and locally available technologies and are also completely dependent on locally available technical personnel.

Greenough and Fuentes (2015) presented energy-efficiency assessment project carried out for a UK manufacturer of ready meals. In this study, building simulation software was used to model the impact of modified temperature control, solar thermal collectors, and absorption chillers on factory energy use. Munguia et al. (2016) presented energy audit report in a meat processing industry. Result of the study showed the potential for energy savings in the selected meat industry.

This study focuses on review of energy usage and energy-saving potentials in food processing industries in Nigeria. The prime objectives of the study are: (i) global overview of performance and energy demand in industrial sector; (ii) to review of patterns of energy and electricity consumption in Nigeria industrial sector; (iii) to assess energy-saving potentials in food processing industries in Nigeria, and (iv) to assess current trends in energy-saving technologies in food industries in Nigeria.

15.2 Global Overview of Industrial Sector

Industrialization involves transformation of raw materials, with the aid of human resources and capital goods into consumers' goods (including food) and new capital goods (Ekpo, 2005). According to Anyanwu et al. in Ekpo (2014), industrialization enhances the utilization of productive inputs (labor, capital, and raw materials), given the country's technology, to produce nondurable and durable consumer goods, intermediate goods, and capital goods for domestic consumption, export, or further production.

Industrialization is often essential for economic growth, and for long-run poverty reduction. Industrial development has had an important role in the economic growth of countries like China, the Republic of Korea (Korea), Taiwan Province of China (Taiwan), and Indonesia. Along with accelerated growth, poverty rates have declined in many countries. Some countries have managed to achieve growth with equity, whereas in others inequality has remained high. As such, the development of industrial sector is required for national development. It has been argued that for a country to have meaningful and sustained development, it urgently requires that it indigenizes its manufacturing, processing, or construction industry, because if industrial sector is inefficient, it will be difficult for such a country to attain meaningful development (Olanrewaju and Abdul-Aziz, 2015).

Furthermore, recent research suggests that economic development requires structural change from low- to high-productivity activities and that the industrial sector is a key engine of growth in the development process. Virtually all cases of high, rapid, and sustained economic growth in modern economic development have been associated with industrialization, particularly growth in manufacturing production. Unfortunately, the state of industrial and manufacturing development in developing countries like Nigeria is weak and has not been improving with time (Tesfachew, 2013).

Manufacturing is an engine of growth due to its potential for employment and productivity growth as a result of learning and specialization effects (Reiner and Cornelia, 2013). Manufacturing remains an essential part of development, but the distribution of value added along value chains suggests that higher value is often associated with pre- and post-fabrication activities such as design or marketing (Baldwin, 2013). Over the last few decades, global manufacturing has shifted from West to East and from North to South. Since the beginning of the century, rapid growth in manufacturing value added (MVA) has been a major source of poverty reduction in many developing and emerging industrial economies (DEIEs) through employment creation and income generation. Those countries still have considerable capacity for manufacturing growth and technological progress in the coming decades.

15.2.1 Global Energy Demand in Industrial Sector

The Industrial revolution (1760–1840) changed the nature of manufacturing processes by using mechanical energy. Machine tools started replacing hand production methods which increased the need for energy (Kanneganti et al., 2017). According to Energy Information Administration (U.S. Energy Information Administration, 2013), the global industrial sector is primarily comprised of manufacturing (food, paper, chemicals, refining, iron and steel, nonferrous metals, metallic minerals, and others) and nonmanufacturing (agriculture, mining, and construction). Each of these industries has different attributes and technologies (Rosen, 2013). The industrial sector is an important end-use sector, since all industrial processes require energy for the conversion of raw materials into desired products. Energy use in industry is much more related to operational practices than in the commercial and residential sectors. Typically, in the industrial sector, the energy flows through the different macrosystem, which can be named as iron-steel industry, cement industry, chemical and petrochemical industry, sugar industry, fertilizer industry, non-iron metal industry, and other industries is shown in Fig. 15.1 (Utlu and Hepbasli, 2007).

The industrial sector accounted for 27% of the total global energy use in 2005 (Banerjee et al., 2012). The total energy use by industry in 2005 was about 115 EJ. The share of final energy use by different industrial sectors in the world is shown in Fig. 15.2. From Fig. 15.2, it can be seen that cement, iron, and steel, chemicals, pulp and paper, and aluminum are key energy intensive materials that account for more than half the global industrial use.

It has been shown that industrial energy intensity (energy use per unit of industrial output) has declined substantially over the last three decades across all manufacturing subsectors and all regions due to improvements in energy efficiency and a change in the structure of the industrial output (Banerjee et al., 2012). In absolute terms, however, energy use and CO_2 emissions have increased worldwide. Industrial final energy use increased 61% between 1971 and 2004, an average annual growth of 2% (Fig. 15.3). But the growth rates are not uniform. For example, in the chemical and petrochemical subsector, which is the largest industrial energy consumer, energy and feedstock use has doubled while energy use for iron and steel production has been relatively flat, despite strong growth in global production.

At world level, the energy intensity of industry (Fig. 15.4) decreases by 1.2%/year on average over the projection period. This means that the

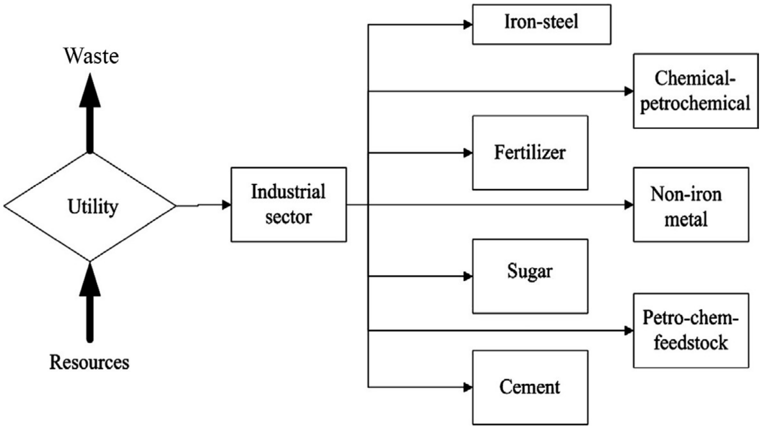

Fig. 15.1 Illustrative presentation of subsystems of the industrial sector. From Utlu, Z., Hepbasli, A., 2007. A review and assessment of the energy utilization efficiency in the Turkish industrial sector using energy and exergy analysis. Renew. Sustain. Energy Rev. 11, 1438–1459.

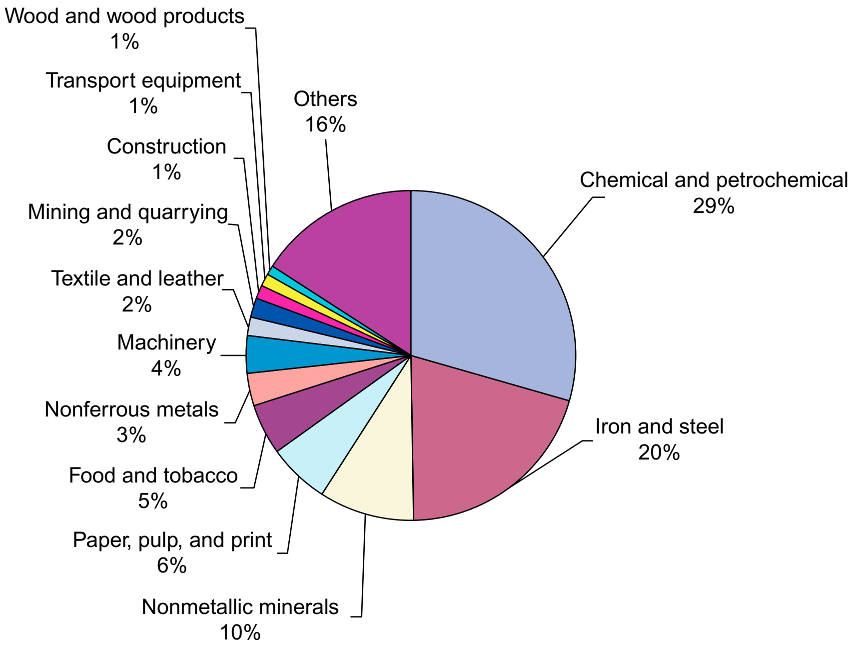

Fig. 15.2 Share of industrial final energy use in 2005. Source: Data based on International Energy Agency, World Energy Outlook 2008, ISBN: 978-92-64-04560-6, IEA, France, https://www.iea.org/media/weowebsite/2008-1994/WEO2008.pdf.

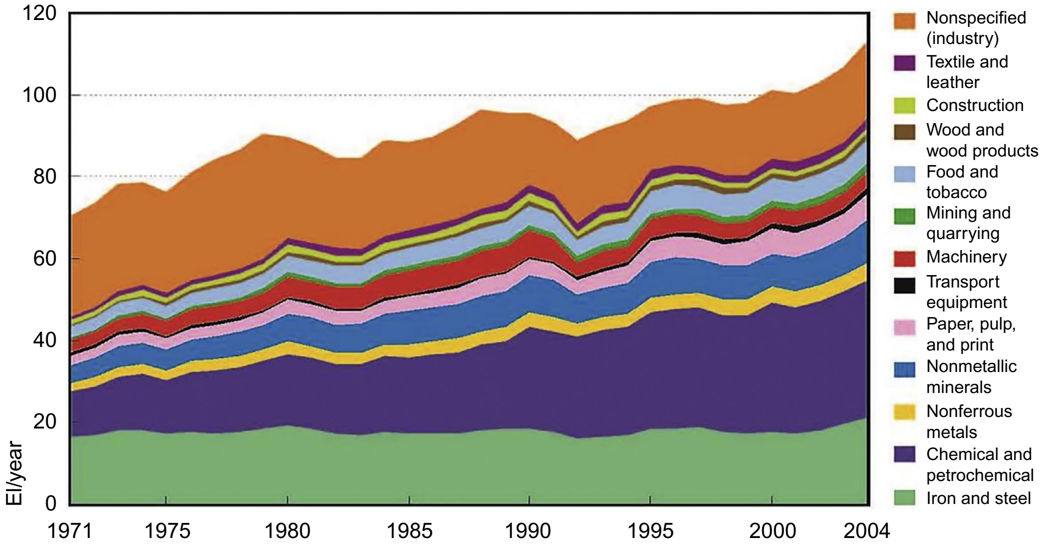

Fig. 15.3 Industrial final energy use, 1971–2004. From IEA, 2006. Energy Technology Perspectives: Scenarios & Strategies to 2050. IEA/OECD, Paris.

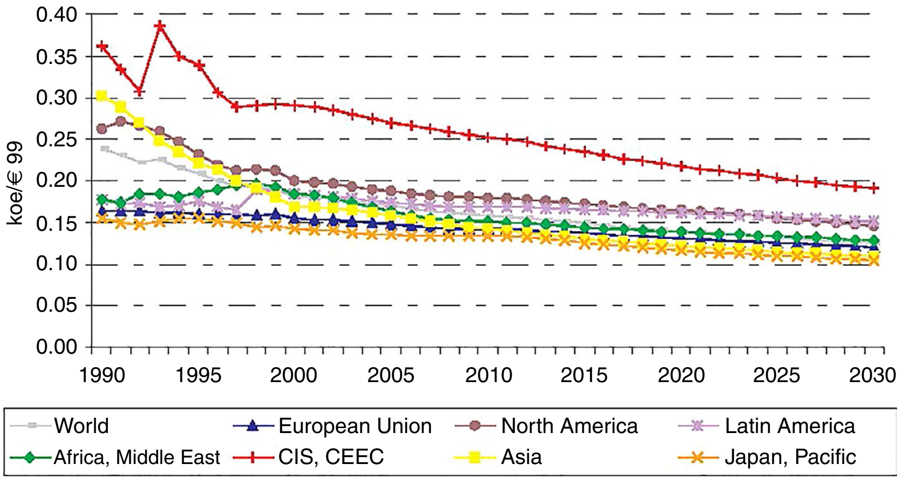

Fig. 15.4 Energy intensity of the industry sector. From Busquin, P., 2003. World energy, technology and climate policy outlook 2030, Belgium, pp. 1–148.

energy productivity of industry is progressing by 1.2%/year: more value added can be produced with less and less energy.The greatest improvements in the energy productivity are expected in Asia (1.5%/year) and in the CIS and CEEC regions (1.4%/year). North America and the Japan and Pacific region are projected to have progression of around 1%/year. The EU, with an annual average reduction of 0.9%, has the slowest energy intensity decrease among industrialized regions (Busquin, 2003).

In 2004, total global primary energy supplied was about 469 exajoules (EJ) (11,213 Mtoe) (IEA, 2006). Industry accounts for nearly one-third of this energy use at more than 147 EJ (3510 Mtoe) including conversion losses from electricity and heat supply. Total final energy use by industry was 113 EJ in 2004. Table 15.1 shows a global breakdown of industrial energy use by fuel and energy carrier in 2004 with CO_2 emissions. The amounts of coal, gas, oil, and electricity used are similar. Combustible renewables and waste is lower and is largely biomass used in the pulp and paper industry.

Nowadays, industrial sector as one of the largest energy consumers takes into account several projects and researches. It was reported that the share of energy consumption of the industrial sector varies between 30% and 70% based on different applications and locations. For instance, the share of energy consumption of the industrial sector of Jordan was reported to be around 31%, 30% for Slovenia, 35% for Turkey, and 70% for China (BoroumandJazi et al., 2013).

Different countries have different mixes of energy supply and sectoral energy use patterns. One of the factors affecting future global industrial energy use patterns is the growth of industry in developing countries. The trends of growth in developing countries and saturation

Table 15.1 Final Energy Use by Energy Carrier, 2004

Energy Carriers	Energy Use (EJ/Year)	Carbon Dioxide Emission (Gt CO_2/Year)
Coal & coal products	28.9	2.72
Natural gas	23.6	1.32
Oil & oil products	28.0	0.73
Combustible renewable & waste	7.0	–
Electricity	21.5	3.59
Heat	4.2	0.29
Process emissions		1.08
Total	113.3	9.73

From IEA, 2007. Tracking Industrial Energy Efficiency and CO_2 Emissions. OECD/IEA, France, pp. 1–234.

Table 15.2 Comparison of Industrial Energy Use in Selected Countries for 2005

Country/ World	TPES (EJ)	Final Energy Use by Industry (EJ)	Electricity Use by Industry (EJ)	Industrial Share of GDP (%)	MVA/ Capita
World	478.9	115	22.2	32	1014
Brazil	9.1	3.3	0.6	15	594
China	72.7	24.6	4.9	34.1	492
India	22.5	5.5	0.8	14.1	80
South Korea	8.9	3.2	0.66	40.3	187
Germany	14.4	2.38	0.83	21.4	5090
United Kingdom	9.8	1.33	0.43	13.6	2683
France	11.5	1.37	0.5	13.94	3291
Japan	22.1	6.3	1.2	22.1	8608
Russia	27.4	7.2	1.2	19.0	461
South Africa	5.3	12	0.4	16.4	550
United States	97.9	16.6	3.3	15.3	5604

From Banerjee, R., Cong, Y., Gielen, D., Jannuzzi, G., Maréchal, F., McKane, A.T., et al., 2012. Chapter 8: End-use efficiency: industry. In: Gomez-Echeverri, L., Johansson, T.B., Nakicenovic, N., Patwardhan, A. (Eds.), Global Energy Assessment: Toward a Sustainable Future. International Institute for Applied Systems Analysis, Vienna; Cambridge University Press, Cambridge, pp. 513–573.

in the energy-intensive industries of developed countries have implications on the future energy mix. Table 15.2 shows a comparison of industrial energy use for selected countries of the world. The MVA per capita, total primary energy supply, and final energy and electricity use by industry are compared for different countries (Banerjee et al., 2012).

In many developing countries energy use are driven by industrialization, urbanization, increasing road transportation, and increasing personal incomes. Energy demand in industry has fallen in most higher-income developing countries, both as a result of higher energy prices in the 1970s and 1980s and open borders to international competition. China has shown the most dramatic developments, but most Latin American and other Asian economies have also shown energy intensity improvements in this sector. In recent years many manufacturers in industrialized nations have moved energy-intensive industries to developing countries, often to take advantage of cheaper labor, less stringent environmental regulation, and lower overhead and transportation costs (Jochem, 2000; Tesfachew, 2013).

15.3 Overview of the Nigerian Industrial Sector

Nigeria's manufacturing sector is one of the major driving forces behind the country's economic growth. In 2013, the manufacturing sector accounted for 9% of GDP (€ 40 billion). From 2011 to 2013, growth in the sector has been rapid at a pace of almost 18% per annum, although it was hampered by supply bottlenecks, including disruptions to the electricity supply. The food, beverages, and tobacco subsector is the largest contributor (50.44%) to the total manufacturing output (Visser et al., 2016). In the food, beverages, and tobacco subsector, the largest contributor to total manufacturing output is sugar manufacturing which constituted 44.20% of the subsector's total in 2012, and contributed the majority of the growth in the entire manufacturing sector at 27.59% in 2012 (NBS, 2014).

Prior to rebasing, manufacturing included just three activities—oil refining, cement, and other manufacturing. In 2013, the other manufacturing activity has been broken down into 11 different activities, bringing the total for the manufacturing sector to 13. Fig. 15.5 shows how total manufacturing output is divided among these activities. Food beverages and tobacco is by far the greatest contributor at N3814.50 billion or 52.74% of the total output. The activities from the old classification of cement and oil refining follow, at N450.75 billion or 6.23% and N412.30 billion or 5.70% of the manufacturing sector total in 2013, respectively.

Between 2010 and 2012, total manufacturing output in the formal sector in Nigeria was dominated by output from the food beverages and tobacco activity, with N4,930,494.55 million or 72.02% of output contributed in 2010. Despite the activity's growth of N488,855.06 million or 9.91% in 2011 and N712,759.35 million or 13.15% in 2012, this total output share declined to 66.32% and 62.42% in 2011 and 2012, respectively (NBC, 2014).

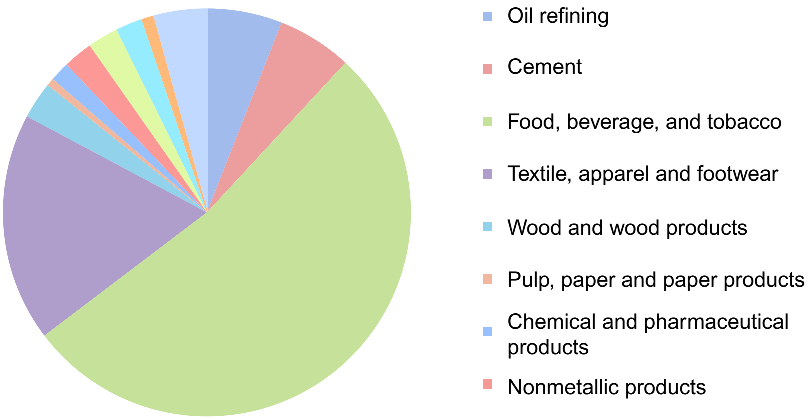

Fig. 15.5 Composition of manufacturing sector in Nigeria in 2013. From National Bureau of Statistics (NBC), 2014. Nigerian manufacturing sector: summary report: 2010–2012.

The largest output of all the manufacturing sector is food, beverages, and tobacco activity with the greatest number of classes of goods captured. Of those product classes, the greatest contributor between 2010 and 2012 was sugar, which had an output of N1,940,413.34 million, N2,438,316.12 million, and N2,710,304.15 million in 2010, 2011, and 2012 respectively, constituting 39.36%, 44.99%, and 44.20% of the food, beverages, and tobacco total in each year. To put this in perspective, the product alone contributed 28.35%, 29.84%, and 27.59% to the total output for the manufacturing sector as a whole in the respective years of 2010, 2011, and 2012. Growth of sugar output was higher than the sector average in 2011, increasing by N497,902.73 million or 25.66%, driving the majority of growth in the sector in that year. With growth of N271,968.03 million or 11.15%, the sheer size of sugar output meant that it largely contributed to the growth seen the following year also. Fig. 15.6 shows output by product: food, beverages, and tobacco activity.

15.3.1 Patterns of Energy and Electricity Consumption in Nigeria Industrial Sector

Electricity systems in Nigeria are epileptic in nature with inadequate generation capacity, low diversity of generation options, and low reliability of transmission and distribution systems. In the country, electricity supply is interrupted for more than 1 h each day. The MAN reported Nigeria System Average Interruption Duration Index (SAIDI) of 60,000 min or greater per annum. This is in spite of the fact that only about 40% of the 150 million Nigerians have access to electricity (Oyedepo and Fagbenle, 2011). Recent survey carried out in the country by GIZ (2015) showed that the total number of electric power

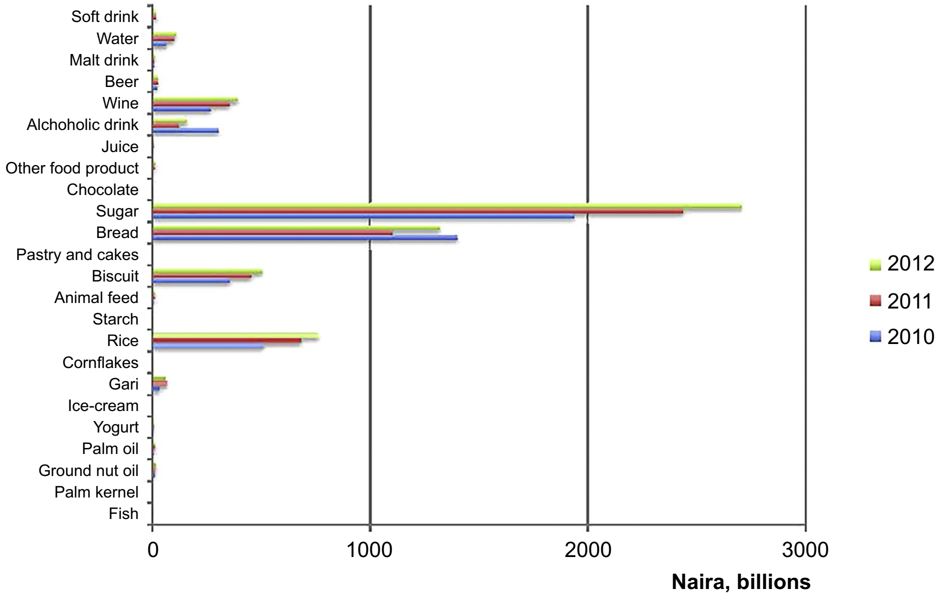

Fig. 15.6 Manufacturing data by products.

outages stood at 197 h per month, compared to 15 and 39 h in the world and Sub-Saharan Africa, respectively. Consequently, all manufacturing firms rely on self-generated electricity to maintain sufficient back up to power their operations in the event of power failure. The development had impacted negatively on the capacity utilization of firms, which had declined from 59.8% in 2014 to 54.2% in second quarter of 2015 and output of firms with attendant loss of revenue. Recently, Nigeria had been able to trace the collapse of her industrial sector, and small- and medium-scale businesses and economic downturn to the inadequate and erratic state of the country's electricity market (Olugbenga et al., 2013).

The Nigerian manufacturing sector is faced with increasingly protracted energy crisis, which has made energy cost a predominant component of the production cost, such that cost of energy accounts for about two-third of the total production cost. This in effect has led to increase in cost of production and lack of global competitiveness of goods produced in Nigeria (Airoboman et al., 2016). Hence, the Nigerian manufacturers are seeking opportunities to reduce manufacturing costs through the use of cost-effective energy-saving technologies and practices that will reduce operating costs while maintaining or increasing product quality and quantity (Fadare et al., 2010; Nwachukwu, 2011; Mbisiogu, 2013; Mgbeokwere, 2013; Chukwueyem et al., 2015).

The poor state of infrastructures in the power sector has been identified as the major cause of stagnant growth of the Nigerian economy.

More than 80% of firms considered power and voltage fluctuations as major obstacles to their smooth operations. Nigeria needs massive investment in the power sector if it is to meet the energy demand of a huge population and power her industrial development aspirations (Oladokun and Asemota, 2015). For manufacturing industries to sustain production, Nigerian manufacturers have resorted to the use of diesel and gas for their energy needs (Ajayi and Ajayi, 2013). Estimates suggest that between 8 and 14 GWh of decentralized diesel generator capacity is currently installed in the country (Visser et al., 2016; Oke, 2006). Fig. 15.7 shows the self-generation in each of Nigeria's manufacturing subsectors. From Fig. 15.7, chemical and pharmaceuticals industry has the highest installed self-generation capacity this is followed by food and beverages industry. On average, about 48% of total electricity consumed annually in the manufacturing sector is self-generated by using diesel generators in which 86% of Nigerian firms own due to electricity outages (Ley et al., 2015).

Fig. 15.8 shows electricity consumption in the major economic sectors in Nigeria. The growing trend for electricity consumption in the residential sector, varies from 3949 GWh in 1990 to 14,549 GWh in 2012. The commercial/public services electricity consumption was 6627 GWh in 2012, while the industrial electricity consumption was

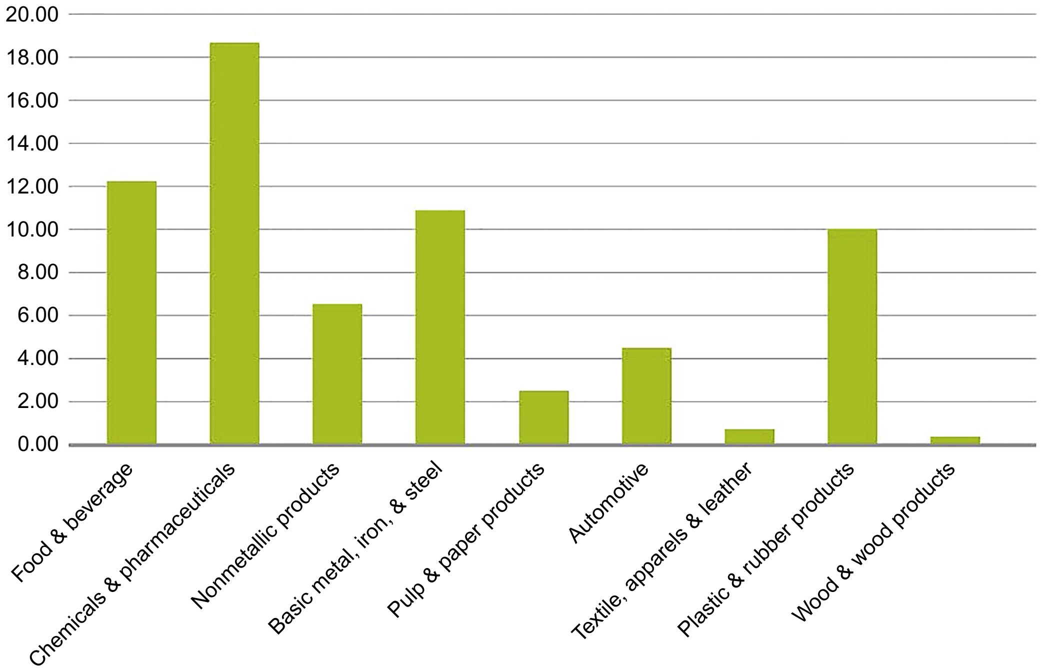

Fig. 15.7 Installed self-generation capacity in Nigerian Industry. From NESP, 2014. Scoping study: energy efficiency in the manufacturing sector in Nigeria. Available from: http://www.energyplatformnigeria.com/images/Library/Scoping_Study_EE_manufacturing_sector_-_GIZ_NESP_2014.pdf.

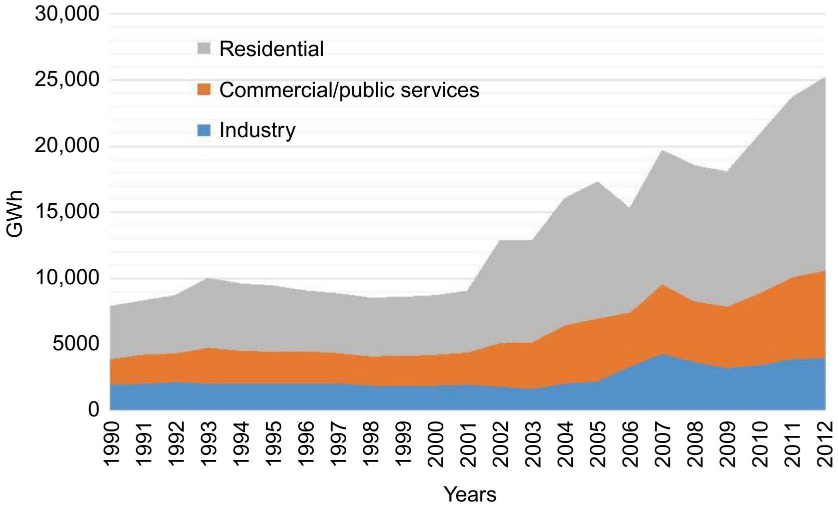

Fig. 15.8 Electricity consumption by sector. From Emodi, N.V., 2016. Energy Policies for Sustainable Development Strategies: The Case of Nigeria. Springer, Springer Science+Business Media Singapore, Frontiers in African Business Research, ISBN: 978-981-10-0973-0, pp. 9–67.

3983 GWh (Emodi and Boo, 2015). Considering Fig. 15.2, electricity consumption in the industrial sector did not increase much in 2012, as compared to 1990. Moreover, it is very clear that electricity consumption in the residential sector is far greater than that of the industrial sector in 2012. This reveals the fact that electricity supply in the industrial sector has been very low and epileptic in nature. This may somehow account for the high rate of unemployment in the nation due to downsizing of most organizations capacity as a result of high cost of production which emanated from low and epileptic electricity supply to the sector. In fact not only small and medium enterprises have been forced to shut down their operations because they cannot cope with the rising cost of production resulting from alternative power generation strategies (Alao, 2016). For example, the South African mobile phone company MTN who operates the largest mobile phone company in Nigeria is estimated to have installed 6000 generators to keep its base station running for up to 19 h a day. This cost the company $5.5 million a month on diesel in order to run the generators (Lawal, 2008).

15.4 Food Manufacturing and Processing Industries—Global Overview

Food processing consists of the transformation of harvested crops, milk and meat products, slaughtered animals, fish, or other food-based raw materials into attractive, marketable, and often long shelf-life food products. It is a multifaceted industry and incorporates processes such as fermenting, sun-drying, preservation with salt, different types of cooking or precooking (such as roasting, smoking, steaming, and oven-baking), and canning among others. It also involves transportation, receipt of raw materials, processing, packaging, storage (both raw materials and final products), and distribution (NTA, 2015).

The food manufacturing industry can be fragmented into various subsectors according to different kinds of food processing and manufacturing methods: bakery manufacturing; confectionery, chocolate and candied fruit manufacturing; instant food manufacturing; liquid milk and dairy manufacturing; canning; manufacturing of condiments and fermented products; and manufacturing of other food (Jianguo et al., 2014). Food manufacturing involves several biotransformation reactions and separation processes, while large amounts of by-products and many kinds of pollutants will be generated in the process, creating huge potentials of developing the circular economy in the sector (Arora et al., 2014).

The food manufacturing industry plays a significant role in every nation economy. It serves not only as a source of employment but also a market outlet and added value for primary agricultural products (Ahmed, 2012). In most of the developed countries, the food processing industry provides an important link between the farmer and the consumer. This industry is vital to assure a uniform supply of foods throughout the year (Aderemi et al., 2009). Operations such as sterilization, freezing, and drying assist in minimizing product losses during handling and storage. During the last several decades, introduction of mechanization to achieve high processing capacity has caused the food industry to depend more heavily on energy obtained mostly from petroleum products (Waide and Brunner, 2011).

Food manufacturing and processing, like other manufacturing segments, is undergoing change. In terms of technology, automation has increased in the industry. Several of the manufacturing processes such as filling bottles, washing vegetables, and fruits, labeling and sealing have become automated. Therefore the skills sets demanded for these processes have moved from manual labor to that of skilled machine operators. Over the next few years there will be a reduction in the demand for manual labor for these processes particularly by large-scale processors (Jianguo et al., 2014).

15.4.1 Energy Use Pattern in Nigeria Food Manufacturing and Processing Industries

Industries generally use various energy sources such as oil, gas, coal, solar, nuclear, wood-fuel, and electricity in the process of their final product. Food industry requires energy for a variety of equipment, such as gas-fired ovens, dryers, steam boilers, electric motors,

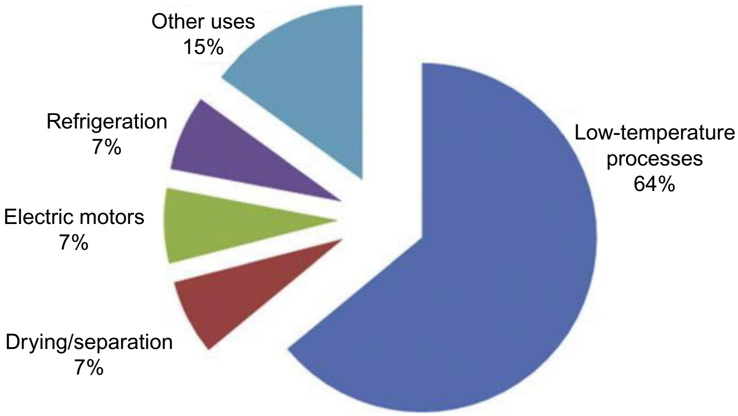

Fig. 15.9 Breakdown of food sector energy use. From Law, R., Harvey, A., Reay, D., 2013. Opportunities for low-grade heat recovery in the UK food processing industry. Appl. Thermal Eng. 53(3), pp. 188–196.

refrigeration equipment, heating, ventilation, and air-conditioning systems. In food industry, the principal type of energy use is electricity. Two-thirds of electric consumption is used in generating mechanical power to operate industrial machineries such conveyors, pumps, compressors, boiler, lightning devices, etc. The food manufacturing companies in Nigeria use electricity for virtually all their daily activities especially in the area of machinery and instrument operation during production. This electrical energy is obtained either directly from national grid or from company's stand-by diesel-powered generating set (Aderemi et al., 2009). Thus, a critical element of the plants energy management involves the efficient control of crosscutting equipment or utilities that powers the production process of the plant. Another important area of ensuring effective utilization of energy in food processing industries in Nigeria is the proper and sufficient operation of the various processes. Process optimization and ensuring the most efficient technology is a key to energy savings in plant's operations.

The industrial processes used in the food industry vary between different facilities and are responsible for most of the energy use. For example, low-temperature heating processes accounting for 64% of all energy uses, while refrigeration and drying/separation account for 7% each (Law et al., 2013). Fig. 15.9 shows breakdown of food sector energy use.

15.4.2 Energy-Saving Potentials in Food Manufacturing and Processing Industries

In industries, several types of applications (motors, boilers, compressors, furnaces, air-conditioning and space cooling, lighting, etc.) use energy in its different forms. An efficient use of these applications can reduce considerably the energy bill and CO_2 emissions in industries (Boharb et al., 2017). Every industrial process is unique and has its own specific areas where energy efficiency can be improved. There are a few common to many industries, which have opportunities for energy-efficiency improvement. All plants are designed with at least one form of energy conversion systems. It is very important that the systems are efficient and reliable and that the environmental impacts are considered (Mossie, 2016).

Research has shown that food industry wastes energy in areas such as boiler plant, service water reduction, air handling system, room conditioning unit self-contained heating ventilation and air-conditioning (HVAC) equipment, building air leakage, poor control and use of sunlight, artificial lighting, independent energy-using components, among others (Utlu and Hepbasli, 2009).

According to Aderemi et al. (2009), adopting the best achievable technology in the food industry can result in savings of up to 10%–30% below the current average costs. The economic payback period for these measures ranges from less than 9 months to 4 years. A systematic analysis of materials and energy flows indicates significant potential savings for process integration, heat pumps, and cogeneration.

Efficient energy utilization in food processing industries is essential because of the following reasons:

- Most energy sources used in food processing industries in Nigeria are nonrenewable, so increasing energy conservation will extend the availability of energy sources.
- Investments in energy conservation measures will provide a better return than investments in energy supply.
- Improving energy conservation will therefore improve the general efficiency of the economy.
- Energy conservation will reduce the negative environmental consequences of energy production and use.
- Cost effective energy conservation techniques can save food processing industries from 10% to 30% of industrial energy consumption.

In Nigeria, energy-saving opportunities in the food processing industrial subsector have remained a matter mirage over the years due to lack of interest at addressing issues relating to energy efficiency and management. Energy efficiency simply means that energy should be used in a manner that will minimize the amount of energy needed to provide required services. This is possible if there is improvement in practices and products being used. In Nigeria food processing industries, a lot of energy is wasted due to usage of more energy than is actually necessary to fulfill their needs. One of the reasons is that old and inefficient equipment and production processes are being engaged. The other reasons are unwholesome practices that lead to energy wastage. In this section, reports of energy audits carried out in some food processing industries in the countries that identified energy-saving potentials are presented as follows:

According to energy audit report of selected industries by Oyedepo (2012), in the beer manufacturing company, it was observed that energy-saving opportunities exist in the following areas: steam loss from deaerator, steam line leakages from joint and holes, exposed steam lines, oversized boiler used in the company, NH_3 pipeline due to thick ice formation, cooling tower, brine motor pump low generator frequency, and low power factor. Oyedepo and Aremu (2013) investigated energy use of food processing industry and distillation and bottling company in Nigeria. The study revealed that the following factors contributed to energy waste and inefficient utilization of energy in the selected companies: poor in housekeeping of cooling space devices (air-condition and fans), refrigeration equipment, and electric motors that dissipate much heat, use of electric motors that are weak and generate excessive heat due to rewound more than twice, improper lagging of boilers that lead to losing much heat, switching on of the lighting points in the day time and generation of electrical energy more than needed in the industry by some electric generator.

Ogunjuyigbe et al. (2015) conducted energy audits for four selected food and beverage industries in Nigeria and found that replacing standard motors with high-efficiency motors and changing existing lighting devices with LED and with LED and compact fluorescent lamp (CFL) were able to achieve a total energy savings of 1,130,115 MWh representing 11.34% of the consumption of motors and lighting in the four audited food and beverage industries.

Apart from above energy audits reports, energy-saving potentials in the following sections are observed in food processing industries in Nigeria:

15.4.2.1 Heating, Ventilation, and Air-Conditioning System

Heating, ventilating, and air-conditioning (HVAC) is the important energy equipment in the industrial sector.

In food processing industries in Nigeria, most of the HVAC equipment used are found dirty and dissipating much heat. In view of this, energy can be saved through:

(i) proper and regular cleaning of the heat exchangers for easy heat transfer;
(ii) proper setting of cooling temperatures to avoid wastage;
(iii) fitting of doors with springs to allow for self-control to trap cold air;
(iv) installation of ventilation system to provide fresh air of constant temperature.

15.4.2.2 *Electrical Drives*

In food industries, electric drives of one type or another use about 65% of industrial electricity, for example, electric motors, compressors, refrigeration systems, fans, pumps, etc. Improvements in these applications would have a significant effect on reducing industrial electrical energy.

In most of the food industries in Nigeria, electric motors used are rewound more than twice, hence they are weak and generate excessive heat. Also, some of the motors are not properly kept. In this regard, some energy can be saved through:

(i) reconfiguration of electrical motors from delta to star connection so as to operate at less than 33% of the rated output;
(ii) replacement of old electric motors with new ones;
(iii) good house-keeping and maintenance of electric drives;
(iv) installation of variable speed drives and soft-start options on electric motors.

15.4.2.3 *Electric Process Heat*

In food manufacturing industries, typical heating applications include resistance heaters (metal sheath heaters, ovens, furnaces, boilers, etc.), electric salt bath furnaces, infrared heaters, induction and high-frequency resistance heating, dielectric heating, and direct arc electric furnaces.

There is much heat loss through steam generators used in the food processing industries in Nigeria due to improper lagging of pipes carrying steam from boiler into the factory. Hence, energy can be saved through:

(i) changing the aging boilers with new and much smaller boilers to reduce energy wastage;
(ii) procuring high-precision burner controls for continuous correct air-fuel ratio management;
(iii) employing recovery measure of flash steam from condensate or low-pressure steam to be used elsewhere;
(iv) adequate lagging of pipes carrying steam from boilers to the factory.

15.4.2.4 *Lighting*

In Nigeria food processing industries, industrial lighting systems are not properly control in the sense that some of the lighting points are always on even though the sunlight is bright enough to provide illumination. In this regard energy use in food industries through lighting can be reduced by:

(i) use of electronic control to conserve daytime power waste for lighting;
(ii) change of lower-efficiency lighting fixtures with more energy-saving types;

(iii) factory walls and ceilings to be painted with white or lighter colors;
(iv) use the light reflectance to improve the brightness of the workplace.

15.4.2.5 Electric Generator

It is common phenomenon in Nigeria food processing industries to have electric generators generating energy more than needed. This leads to energy wastage and high cost of production. Inefficient energy utilization can be minimized by:

(i) using generator having capacity to meet the needs of the industry;
(ii) changing diesel electric generator to gas generator. As gas is abundant and cheaper in Nigeria.

Internal Transport

Internal transport (within the industrial site) generally accounts for a fairly small portion of the energy and electricity used in industry. Possible means of improving the energy efficiency of internal transport include:

- converting from diesel and gasoline vehicles into more energy-efficient ones (e.g., electrically powered);
- maintaining adequate tire pressure;
- improving production planning to reduce transport distance;
- optimizing storage location to reduce transport distance.

Compressed Air

In food processing industries, air compression, in which compressors are a major component, accounts for about 17% of global industrial electricity use. Means of improving the energy efficiency of air compression include:

- reducing air leaks (easy measure with short payback period);
- reducing air pressure from 7 to 6 bars (approximately 7% energy reduction per bar);
- using VSD compressors;
- considering the possibility of using the compressor's cooling output for space heating purposes.

Energy loss and loss and cost of energy consumption in the food processing in Nigeria can be abated by:

- constant monitoring of energy use in the factory with the state of art equipment;
- significant capital investment to improve the energy consumption;
- constatnt and detailed energy audit to identify the causes of energy wastes;
- proper maintenance and control to improve the energy productivity.

15.5 Possible Energy-Saving Technologies in Nigeria Food Processing Industries

Energy efficiency is a means of using energy more efficiently, either through change of behavior, improved management or the introduction of new technology. Through efficient utilization of energy in food processing industries, energy demand can be reduced without reducing structural changes or adversely affecting economic growth (Mossie, 2016).

Energy-saving potential in the food industry in Nigeria can be achieved with the following approaches:

(a) Improving the efficiency of the conversion processes in various operations through different techniques; these include:

- Waste-heat recovery from plant equipment
  Waste heat recovery is a way to reduce energy consumption in industry (Brückner et al., 2015). In food industry, waste heat is available at low temperatures. Among the available technologies to capture the waste heat include: on-site recovery from a heat source to a lower grade sink using a heat exchanger, temperature uplift from a heat source to a higher grade sink using a heat pump, using heat for refrigeration via an absorption chiller, conversion of heat to power using the organic Rankine cycle (ORC), feeding waste heat into a local heat network for use somewhere else (Law et al., 2013; Berthou and Bory, 2012). This waste heat can be recovered and reused in other processes onsite (to preheat incoming water or combustion air, preheating furnace loads, etc.), or transformed into electricity, cold, or other type of heat (Miró et al., 2016).
- Combined heat and power system
  Combined heat and power (CHP) systems reduces the overall energy intensity of industrial systems. Bottoming CHP cycles can be used in food processing industrial facilities as these industries often have high-temperature waste streams that are favorable for waste heat recovery. The overall energy efficiency of food industrial processes can be improved by capturing and reusing the waste heat through bottoming cycle.

(b) Improving use of energy efficient or premium efficient electric motors
According to Mossie (2016), replacing failed electric motors with energy-efficient or premium-efficient electric motors; scheduled and proper greasing of electric motor bearings, reducing electric motor system friction losses, properly sizing electric motors to the load; testing questionable equipment before and after repair, improving the fuel consumption efficiency, improving lighting systems; and other measures that can be immediately implemented

or implementation plan after energy losses assessment are very important steps to improve the food industries over all energy efficiency in food processing industries.

(c) Use of improved or additional equipment such as multiple effect evaporators, mechanical vapor compressors, ring driers, screw, and pneumatic dewaterers before drying, matched air compressors, microwave driers, and cookers to eliminate long steam heating, agitators in the vacuum pan of evaporators, and a scraping device in evaporation to improve heat transfer.

(d) Development of alternative technologies that are more energy efficient in terms of quantum of consumption, cost, and use of scarce energy sources.

Development and use of alternative technologies based on less energy consumption can be a better proposition for Nigeria which is on the threshold of industrialization, since this option gives sufficient opportunity to use scarce resources more judiciously. While less expensive techniques for energy savings in the existing food industry can be made acceptable by governmental regulatory mechanisms, their enforcement on a national scale becomes an impossible task. The availability of viable technologies with lower energy requirements can be of considerable significance to the development of food processing industries in Nigeria.

15.5.1 Benefits of Utilizing Energy-Saving Technologies in Food Processing Industries

The food processing industries are very energy intensive. Effective utilization of energy use in the industries saves money, enhances corporate reputation, and helps everyone in the fight against climate change. Table 15.3 presents the benefits from efficiency improvements in food processing industries.

Improved energy system efficiency can also contribute to an industrial facility's profitability at the same time as improving the reliability and control. Increased production through better use of equipment assets is frequently a collateral benefit. Maintenance costs may decline because better matching of equipment to demand results in less cycling of equipment operation, thus reducing wear. Optimizing the efficiency of steam systems may result in excess steam capacity that can be used for CHP applications. Payback periods for system optimization projects are typically short—from a few months to 3 years—and involve commercially available products and accepted engineering practices.

Understanding these benefits and properly incorporating them into cost analyses is important because these improvements can significantly change the cost assessment of the technology and result in a more favorable evaluation.

Table 15.3 Non-Energy Benefits From Efficiency Improvements in Food Processing Industries

Waste	Emissions	Operation and Maintenance
Use of waste fuels, heat, and gas reduce: product waste, waste water, hazardous waste, and material reduction	Reduced dust emissions; reduced CO, CO_2, NO_x, and SO_x emissions	Reduced need for engineering controls; lowered cooling requirements, increased facility reliability, reduced wear and tear on equipment/machinery, and reductions in labor requirements

Production	Working Environment	Other
Increased product output yields; improved equipment performance; shorter process cycle times; improved product quality/purity; and increased reliability in production	Reduced need for personal protective equipment; improved lighting; reduced noise levels; improved temperature control; and improved air quality	Decreased liability; improved public image; delaying or reducing capital expenditures, increased profits; and improved worker morale

15.5.2 Barriers to Implementing Energy-Saving Measures in Food Processing Industries in Nigeria

The major barriers militating against the implementation of energy-saving measures in food processing industries in Nigeria can be identified as follows:

- Lack of measures to promote energy efficiency in food processing industries

  A package of measures to promote energy efficiency in food processing industries in Nigeria is lacking. Unavailability of long-term financial capital is a major obstacle to the implementation of energy-saving technologies in Nigeria. Stringent bank policies that offer short-term credit loans with high interest rates have contributed to this situation. Under these circumstances, the government ought to provide enabling conditions to increase the availability of investment resources for businesses using financial instruments such as tax exemptions, accelerated depreciation, target bonds, and grants for R&D. The law on energy efficiency contains a number of measures, but they are not sufficient. A possible solution could be equal cofinancing of projects by municipal authorities. In this case companies could take smaller loans, the payback period would be shorter and the modernized system would be able to work at least 5 years without additional investments.
- Minimum energy performance standards for industrial machines

There are no energy-efficient standards for industrial machines, for example, electric motors that are major energy consumers in food manufacturing industries in Nigeria.

- Lack of financial policies that promote energy-efficient investment
  Financial policies that promote energy-efficient investment are missing in Nigeria. The Federal Law on Energy Efficiency establishes energy audits and the issuing of energy passports by all utilities, energy suppliers, and public bodies and authorities as a key energy-efficiency measure. Mandatory energy audits are indeed one of the basic and most effective tools to increase energy efficiency. However, in Nigeria, this process almost completely failed for various reasons, the most important one being that the passports were considered to be a final goal and the government did not develop any clear further plans on measures to be implemented after the energy audits were made and the passports were issued.
- Lack of adequate institutional frameworks
  There is no agency for formulating, coordinating, implementing, and monitoring energy conservation policies and programs in Nigeria.
- Lack of incentive measures on energy efficiency
  In the industry sector there is no long-term government policy on energy efficiency. The current legislation in Nigeria does not compel or incentivize companies to use this standard. Voluntary or long-term agreements between the government and business did not find much support among businesses. Thus, Nigerian energy-efficiency measures in industry do not live up to the IEA recommendations. In Europe and in the United States much more attention is paid to this sector.
- Lack of information
  Awareness of the benefits of adopting energy-saving technologies is relatively low among Nigerian manufacturers. Apart from this, there is no database of energy use in the sectors of the economy.
- Capacity barriers
  Trained manpower to evaluate, certify, implement, and enforce energy-efficiency measures in Nigeria industrial sector is grossly inadequate. Skills for analyzing energy performance, developing energy management systems, and implementing energy efficiency measures are rather rare.
- Low capital availability
  There exists low capital investment on related energy-efficiency measures among most Nigerian manufacturers.
- Regulatory barriers
  There are no codes and regulations to groom energy-efficiency programs in Nigerian manufacturing sector. Moreover, energy policies and promotional schemes usually prioritize the expansion of the installed generation capacity instead of promoting energy efficiency.

- Low quality of equipment
  The Nigerian market is flooded with all kinds of second-hand appliances, underdeveloped quality infrastructure without efficiency labels. They are relatively cheaper compared to the new ones. Many Nigerians are on the opinion that second-hand products are more durable than the new ones. Some of these second-hand products come from industrialized nations and they may have been manufactured long time ago. The efficiency of these products is quite doubtful and the possibility exists that they may have been rejected by the former users to purchase more recent and efficient appliances. Such low-quality equipment hinders wide-spread use of energy-saving technologies in food processing industries in Nigeria.

15.6 Conclusions

In this study, a comprehensive review of energy use pattern and energy-saving potential in food processing industries in Nigeria has been carried out. The study identified areas of inefficient energy use and possible strategies for energy savings in the food manufacturing industries. The major lapses in energy use as identified in this study are: lack of good energy conservation practices, leakages of fuel and steam from fuel or steam pipeline, and use of second hand and aging machines/equipment.

From this study, the followings can be concluded:

(i) Electric motors account for over 65% of electrical energy consumption in food industries in Nigeria, hence improving energy efficiency from the point view of high-efficient electric motors selection will significantly improve the electrical energy utilization for the industry.

(ii) Energy saving of the order of 10% can be achieved in food processing industries by adopting appropriate technology for lighting fixtures.

(iii) Huge amount of heat energy generated as by-products can be reused through waste heat recovery technologies. Such waste heat recovery principle can account up to about 15% energy saving in the food industries in Nigeria.

(iv) Energy waste in food industries in Nigeria can be attributed to lack of diligence, commitment, and readiness of company workers to compliment management efforts in training them. For example, if leaking valves, faulty steam traps, inoperable thermostat controls, lubrication of bearings, motors, conveyor belts, cleaning of lamps' reflecting surfaces, which indirectly result in additional costs could be attended to in time; those additional costs could be eliminated or reduced to the barest minimum.

The antidote over worldwide energy crisis and environmental degradation is energy conservation principle. In particular, Nigeria as a developing country is ready and interested in increasing awareness of inefficient power generation and energy usage. However, the available information on the efficient energy technology is scanty.

The know-how on modern energy-saving and conservation technologies should, therefore, be disseminated among government agency, industrial managers, and policy makers as well as engineers and operators at the plant level in Nigeria. It is particularly important that there is need to acquire practical knowledge of the currently available energy conservation technologies and techniques in food processing industries.

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