Ingegerd Rosborg
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Drinking Water Minerals and Mineral Balance

Importance, Health Significance, Safety Precautions

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Minerals in Water: A Win-Win Issue for Public Health

In the early twenty-first century, drinking water security is rightly a global concern, as hundreds of millions of people still lack daily access to clean and safe drinking water. The increasing risks of climate change have brought us to the awareness that in many regions of the world, water security is under increasing threat and cannot be taken for granted. In more and more locations, people are drinking water that has been treated and recycled from lower-quality water or seawater, while conversely the sales of bottled mineral water are skyrocketing.

Water is essential for life and health, with each adult human being needing to drink on average at least 2 L of water per day to maintain optimum fitness and alertness. Water safety is generally linked with the absence of disease-causing bacteria or pathogens. Yet it is not only the water itself that is crucial to our well-being – the minerals it contains are also vitally important. We talk of “hard” water (which contains high levels of minerals) and “soft” water (which is more acidic). Yet how much do we really know about the mineral constituents of water? Do we have the public health guidance that we need regarding minerals in water? Are water providers paying sufficient attention to these minerals, and do they need to be better regulated? These are the questions which this book goes a long way towards answering.

The health-giving effects of highly mineralized water, found in spas, have been known for thousands of years, certainly since Roman times. Over time, the dangers of high levels of certain elements in water have also become apparent, with tragedies such as the arsenic present in the drinking water wells of Bangladesh causing widespread illness and death. Arsenic toxicity in drinking water is now declared by the WHO as a public health emergency, which has affected more than 130 million people worldwide. Guidelines have been developed with maximum recommended levels of a range of minerals in water. In general, toxicity levels of minerals with regard to human health are now quite well known. However, the beneficial health aspects of minerals in water have not been investigated to the same extent. Broadly, many elements may be beneficial and even essential to health in smaller quantities, and yet harmful in large quantities.

In this book for the first time, we are given an excellent overview of minerals in water and their effects in humans and animals. The interactions between the elements are well described, and this is also crucial in determining their health-giving and harmful effects. For instance, many people are aware that calcium is the most abundant element in the human body and that it is essential for building healthy and strong bones and teeth. Yet how many know that it acts as an antagonist to magnesium, which is essential for a healthy heart? Too much calcium prevents the uptake of magnesium, and hence, the optimum balance of these two minerals in the water which we drink is vital to our health. Bicarbonate ions are the body's most important buffer against acidity. Bicarbonate ions in water help to reduce osteoporosis and have a strong association with increased longevity, in areas where the water is hard (and bicarbonate alkalinity is high). Together with sodium, potassium and sulphate, these are the macroelements, for which there is a great deal of evidence with regard to health impacts.

The microelements or trace elements, such as selenium, lithium, zinc, fluorine, chromium, silicon, copper and boron, are less well understood, and there is so far less evidence regarding the roles that they play. Selenium deficiency has been implicated in a range of diseases, including some cancers. Zinc is essential for healthy growth and a well-functioning immune system. Lithium is protective against several mental health disorders, while boron has been shown to play an important role in joint functioning, and so an optimum level of boron can be helpful against arthritis. The essential role of fluoride in protecting the teeth is of course well known. However, much more research and subsequent regulation are needed regarding the other microelements.

The issue of minerals in water is becoming increasingly important as freshwater resources shrink, while ever-growing numbers of people become reliant on treated and recycled water. Water that has been treated by reverse osmosis or distillation is "demineralized", and drinking such water over a period of time can lead to serious health effects, as has been the case, for example, in Jordan. However, such treated drinking water can quite simply be remineralized to the benefit of the population which is dependent upon it.

Our current drinking water regulations focus on the maximum allowed levels of bacteria and toxins. However, with regard to mineral balance, it is just as vital that the levels of minerals are properly regulated with regard to both maximum and minimum levels and to the ratios among the various elements. Safe remineralized water provides a win-win situation for public health – people are protected against harmful elements in the water while being provided with the balance of vital elements which go a long way towards promoting well-being and longevity. Around the world, we need increased policy awareness of this issue, with the development and enforcement of regulations which will provide us with clean, safe, remineralized water.

Global Water Partnership (GWP) Ania Grobicki
Stockholm, Sweden

Preface

During the last part of the twentieth century, northern Europe, the south western parts of Norway and Sweden, suffered from "acid rain". Sulphur dioxide emissions from combustion of coal and oil on the European continent and the British Islands were dissolved in clouds forming sulphuric acid that hit the Nordic countries, and especially harmed parts having bedrocks and soils of low base mineral content. The consequences were devastating; crayfish in lakes in barren districts were close to complete extinction, fish did not reproduce properly, trees in the forest were damaged, and well waters became more acid. Nutrient minerals, like sodium and potassium, calcium and magnesium, were washed out from soils, when pH values drastically fell as the alkalinity (HCO_3) dropped, while concentrations of aluminium and other toxic elements increased. Acid well water dissolved copper from pipes, and the intestinal bacterial flora was damaged, causing diarrhoea to infants fed with infant formula prepared on the water. The environment and sensitive individuals had lost their mineral balance, as nutrient elements had decreased and toxic elements increased. Editor Ingegerd Rosborg, Sweden, living in a highly affected area, then realized the importance of a steady neutral pH of the environment and body, as well as optimum intake of essential minerals. This led to a PhD in "Mineral element contents in drinking water – aspects on quality and potential links to human health".

In 2010, drinking water scientists and practitioners from different countries of the world gathered on a conference in Kristianstad, Sweden. About 20 participants decided to write a monograph on the importance of minerals and mineral balance in drinking water. Ten proceeded and fulfilled the project in 2014. The first edition of the monograph has attracted high attention and was translated into Chinese (2016). This is the second, revised edition that further deepens the subject of the importance of minerals from drinking water, as new scientific studies and a few more relating elements are included. Additional studies of negative health effects of RO (reverse osmosis), desalinated, water are presented.

This monograph is intended as a course literature at the university level in different educations: environmental sciences, health protection, medicine, toxicology, hydrology, hydrogeology, medical geology and drinking water engineering/production. In addition, the monograph is a good guide for private and public drinking water producers on how to preserve or improve the mineral content and mineral balance of specific drinking waters supplied. It is also a valuable guide for the public in understanding and evaluating the health significance of specific tap or bottled waters, since health supporting ranges of elements and element ratios are presented, for both tap water and bottled water.

The first chapter is a historic introduction to minerals from drinking water, followed by a comparison of minerals from drinking water with the daily intake. The following three Chaps. 3, 4 and 5, give a summary of 48 nutrient and toxic elements in water and their influence on the human body and health. In Chap. 6, the mineral content and mineral balance in non-corrosive water is presented as well as the effects of different water treatments on mineral content and balance. The potential health effects of demineralized water and the importance of mineral balance in drinking water are mirrored in Chaps. 7 and 8. Optimum concentration ranges and element ratios are presented for tap water and bottled water. Future drinking water regulations are suggested in the last Chap. 9. Ions are, in general, presented without charges and may also appear in water as complex ions.

Abstract

Drinking water is necessary for life, our most important food item, and for intake, it has to be microbiologically safe and free from pollutants and toxic substances. In addition, it can provide us with essential minerals, different amounts from different water sources. Unhealthy constituents of concern are included in the WHO, EU and US EPA Guidelines for drinking water quality, as well as constituents that may increase corrosion or cause scaling on pipes or discolouring of cloths. However, the essential minerals in drinking water are important for the human and animal health, since they appear in ionic form and are generally more easily absorbed in the intestines from water than they are from food. Both macroelements from drinking water, e.g. calcium (Ca), magnesium (Mg), bicarbonate (HCO_3) and sulphate (SO_4), appearing at mg/L concentrations, and microelements, e.g. lithium (Li), molybdenum (Mo), selenium (Se) and boron (B) at µg/L, can substantially contribute to the daily intake. Mineral water is even to prefer as a source of minerals compared to mineral supplements, as one doesn't have to remember to take a pill containing the required daily amount. Drinking water is especially important if normal diet does not provide essential minerals in sufficient amount.

Numerous scientific studies clearly show that hard water, with high concentrations of Ca, Mg, HCO_3 and SO_4, is protective against cardiovascular diseases. Hard water is also found to be protective against osteoporosis, decreased cognitive function in elderly, decreased birth weight, cancer and diabetes mellitus. Mg is in many studies identified as specifically important.

Other studies indicate that areas with elevated lithium (Li) in drinking water have lower suicidal behaviour in people with mood disorders and less severe crimes. In areas with high selenium (Se), cancer frequency is lower, and bone and joint

deformities and heart diseases are less common. Optimum fluoride (F) levels in drinking water are favourable for good teeth, but too high concentrations can cause discolouring on teeth and even bone deformations. Studies also indicate that there is a beneficial effect of B in drinking water when the concentration is less than 1 mg/L and chromium (Cr) (III). Goitre is uncommon in areas where the concentration of iodine (I) is >50 μg/L.

On the other hand, a number of negative health effects of toxic elements in drinking water are reported. Thus, aluminium (Al) in drinking water has been suggested as being connected to Alzheimer's disease and dementia. Ingestion of high levels of arsenic (As) is linked to skin disorders and cancer, especially skin and lung cancer. Lead (Pb) in drinking water can severely negatively affect the IQ of children and cause hyperactivity, depression and, if present in higher concentration, disturbed blood formation. Iron (Fe) and copper (Cu) are important nutrient elements, but excess Fe and Cu from drinking water may cause intestinal disorders. Uranium (U) and cadmium (Cd) can disrupt kidney function, but if there is a substantial concentration of antagonistic elements like Ca and Mg, the toxic effect may be reduced. Thus, if water contains Pb, Cd or U, the Ca and Mg should not be eliminated by treatment methods like ion exchange softening, as removal of these elements would increase the negative effects from Pb, Cd and U, which are not removed by especially ion exchange softening. Such aspects are included in the term "mineral balance".

Reverse osmosis (RO) treatment causes completely demineralized water, which is corrosive and may not be suitable as drinking water. Thus, "water intoxication", or delirium caused by hyponatremia, may occur following intense physical efforts, like a marathon or working hard, and ingestion of several litres of low-mineral water. Early symptoms include tiredness, weakness, headache, brain oedema, convulsions and, in severe cases, coma and finally death. Drinking low-mineral water in the long run will increase the risk of acidosis; acidified tissues, as indicated by $pH<6$ in urine; and lowered thyroid function. Acidosis may be a precursor to many diseases, e.g. cardiovascular diseases, diabetes, osteoporosis and cancer. Declining dental health was reported from populations consuming desalinated water, due to low Ca and F levels in water, and there is an increased risk of osteoporosis if low Ca intake via water is not balanced by food. Attempts have been made to evaluate the public costs when a city exchanges a hard and mineral-rich groundwater with desalinated water. The costs were extremely large.

RO water should always be remineralized to at least the minimum levels of the presented ranges in this monograph of the macro constituents Ca, Mg and HCO_3 when it has been produced to be drinking water. Remineralization with, for example, calcite-dolomitic limestone free from toxic elements is preferable for remineralization.

Softening treatment can also reduce the Ca and Mg content to almost zero. In addition, softening filters working as ion exchangers based on sodium chloride, NaCl, increase the Na concentration of the water. High Na levels may contribute to elevated blood pressure. Any treatment to decrease hardness should not be performed

Table 1 Suggested desirable ranges of some macromineral nutrients in drinking water

Parameter	Range	Unit
pH	7–8.5	
Calcium	30–80	mg/L
Magnesium	10–50	mg/L
Bicarbonate	100–300	mg/L
Sulphate	25–100	mg/L
Fluoride	0.5–1.0	mg/L
Chloride	20–50	mg/L
TDS (total dissolved solids)	100–500	mg/L

to lower hardness than 8–10 °dH, Ca ≈50 mg/L, Mg ≈10 mg/L, absolute minimum 5°dH.

In this monograph, a holistic approach for drinking water is presented, as the range of concern is extended from standards for undesirable substances to basic mineral composition of water. Thus, in addition to standards that establish the upper limits for intake, there are also suggested minimum concentrations for elements and ions that can be considered as nutrients (see Tables 1 and 9.2, 9.3, 9.4, 9.5 and 9.6 for bottled water). Desirable ratios between some elements are also suggested. Recommended mineral concentration ranges and ratios are set at levels that cannot imply any health risks, even if food habits and other lifestyle questions are reflected. All these aspects are reflected in the term "mineral balance" of drinking water.

Standards should be followed, first of all, but in an era when the public becomes more and more aware of the importance of minerals and their relations to each other, extensive water analysis should always be performed and the mineral content should be presented to consumers of public drinking waters and stated on bottled waters. Full analysis is also needed before selection of water source, and water source with the best mineral content and mineral balance should be chosen if there are more options available. For treatment of water, one should choose methods that preserve or improve the mineral composition and mineral balance and avoid elimination of elements that act antagonistically with toxic elements. Alkaline filters, used to increase pH for corrosion purposes, should not apply sodium hydroxide (NaOH), since only Na and alkalinity (only slightly) rise. The use of a high-quality calcitic-dolomitic limestone (with minimum toxic elements content) should be preferred. However, it's hard to increase desirable essential elements to minimum recommended level with the use of present technical methods.

This monograph aims to contribute to the knowledge used for revision of the European Drinking Water Directive, EPA Drinking Water Regulations and the WHO Guidelines for Drinking water Quality.

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The writing of the second edition of this book has been very interesting and inspiring but also time-consuming. It has therefore been necessary to have had a good working relationship. To have good working team was vital and very helpful. We would therefore like to thank cordially all the cowriters.

Contents

Chapter 1
Background

Ingegerd Rosborg, Frantisek Kozisek, Olle Selinus, Margherita Ferrante, and Dragana Jovanovic

Abstract Minerals and drinking water play an important role in the body. There are around 20 essential minerals for humans. Their origin is mostly the bedrock, and they can all be present to high or low concentrations in ground as well as surface water. Normal weight adults need 2.0–2.5 L/day of water for proper hydration, and it is known for centuries that water can be a source of minerals, where they are present as ions, in general readily absorbable. In the eighteenth and nineteenth century well off people in Europe went to health resorts to drink specific mineral waters containing sufficient levels of one or more essential minerals, water chosen for a specific health disorders. On the other hand, case histories from alpine climbing or polar expeditions which used melted snow as the only source of drinking water, with no minerals at all in it, appeared in scientific literature in mid twentieth century. The symptoms were derived from acute water and mineral imbalance and water intoxication, and include weakness, fatigue, convulsions, unconsciousness, and even death. Such water is comparable to RO (Reverse Osmosis) treated, desalinated water of today. Low levels of specific mineral elements have been proven to cause some diseases and symptoms. Thus, districts of Norway had high frequencies of softening of bone tissue among domestic animals (later identified as P deficient soils and water), and parts of China had increased levels of heart failure (low Se in

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soils and water). Dental remains of Native Americans from parts of Kentucky indicate Mn and Zn deficient soils and water, as cultivated maize had extremely low levels. During the twentieth century, hard water, with elevated levels of especially Ca, Mg and HCO_3, presently with focus on Mg, is proven protective against diseases, especially cardiovascular diseases, but also diabetes, osteoporosis and even cancer.

1.1 Drinking Water – General Importance of Sufficient/Optimum Intake for a Good Health

F. Kozisek and I. Rosborg

> "Water is a substance, a beverage, a nutrient, and a potential source of other nutrients. It is essential for all forms of life and yet, conversely, is associated with disease and death when insufficient or acting as a vector for pathogens and toxic chemicals." (Grandjean and Bartram 2011).

Keeping proper body hydration is a key factor in maintaining physical and mental health and performance, as well as, to prevent a number of diseases and uncomfortable symptoms. Water is the main constituent of the human body and serves as a universal solvent and mediator of all chemical reactions of organisms. Water also delivers nutrients and aids in the transports of wastes, aids in regulating the body temperature, forms lubricating fluids in joints and the digestive tract, helps to maintain the body structures and supports a number of other functions. The adult organism consists of 50–60% of water, newborns even up to 75–80% of the body weight (Grandjean and Campbell 2004, EFSA 2010).

On average, an adult person daily discharges approximately 2.5 L of water through urine, faeces, breath and skin. However, the organism needs balanced water turnover and has to take water to cover the losses. About 300 mL of "new water" is created through metabolic activity and about 900 mL is obtained from food. This means that the rest, about 1300 mL, has to be consumed in the form of liquids (EFSA 2010, Sawka et al. 2005).

There are several general recommendations about adequate water intake, which may be related to food energy intake (such as from 1.0 mL/kcal (adults) to 1.5 mL/kcal (children) (FBN 1989), or expressed per kg of body weight, or just per day (according to sex and age) as defined by the European Food Safety Authority (EFSA): adequate intakes are 2.0 L/day for adult females and 2.5 L/day for adult males. The EFSA reference values for total water intake include water from drinking water, beverages of all kinds, and from food moisture content and only apply to conditions of moderate environmental temperature and moderate physical activity levels (EFSA 2010).

Nevertheless, it is necessary to emphasize that the water requirement is a strictly individual issue, which is dependent on a number of internal and external factors like body weight, age, sex, composition and amount of food, physical activity, clothing, environmental temperature and humidity, adaptation, present health status etc. (Grandjean and Campbell 2004, Sharp 2007). It means that there are substantial physiological individual variations in water needs (ranging from about 1 to 5 L per day) as well as individual variations over time. One has to continuously seek for his/her own optimum water intake. Infants and young children need water and essential minerals more than adults in relation to body weight, especially premature or low birth weight infants or those suffering from diarrhoeal disease (Grandjean and Campbell 2004, Manz 2007a, b). In addition, the elderly and infirm often do not consume sufficient water or other fluids and can become dehydrated with significant adverse health consequences (Grandjean and Campbell 2004, Volkert et al. 2005) (Fig. 1.1).

Inadequate intake of water may cause or trigger a number of health or well-being related problems of acute or chronic character, with severity corresponding to the level of dehydration or hyper-hydration. Acute signs of dehydration range from headache, fatigue, decline in physical and mental performance (concentration), exercise asthma to hyperthermia and circulatory collapse (Manz 2007b, Ritz and Berrut 2005).

Mild, but long term dehydration, which may be easily overlooked as thirst is not the first and earliest sign of dehydration, can result in fatigue, constipation and a number of more serious pathologies, like nefro- and urolithiasis, urinary tract infections, hypertension, venous thromboembolism, coronary diseases, gallstones, glaucoma etc. (Manz 2007b, Manz and Wentz 2005). Others have cautioned as relevant higher risks of diseases such as Parkinson's disease (Ueki and Otsuka 2004).

Fig. 1.1 On average an adult individual, 70 kg needs to drink about 2 L of fluid per day (Photo: Rosborg I)

Although various stages of dehydration are much more common, one should not forget the health risk of the opposite condition – over-hydration (hyper-hydration), occurring when a hypotonic fluid, especially like RO (Reverse Osmosis) treated, desalinated, water is consumed in amounts that exceed the kidney's ability to excrete the excess water and manifesting as hypo-natremia, also referred to as water intoxication, which can be acutely life threatening (Grandjean and Bartram 2011, EFSA 2010, Habener et al. 1964, Keating et al. 1991).

A lifetime daily water (liquid) consumption of 1.5 L represents about 40,000 L (medium swimming pool). It is then not surprising, that not only continuous adequate intake, but also the quality of water (liquids), including its mineral composition, may have an important impact on the health status of the organism (Grandjean and Bartram 2011).

The taste of water is important to encourage drinking, especially in individuals who have lost the thirst. The amount of TDS, Total Dissolved Solids (Ca, Mg, Na, Cl, K, SO_4 and HCO_3), and hardness, especially Ca and Mg, has effect on taste of water. Water with low TDS is flat and insipid while with high TDS (>2000 mg/L) become objectionable and unpalatable. The palatability, taste of the water, with TDS level up to 600 mg/L is considered good. TDS in desalinated, Reverse Osmosis treated water is often 1 mg/L, and the conductivity <0.1 mS/m (Kozisek 2005).

1.2 Early and Recent Discoveries of the Influence of Minerals from Locally Cultivated Crops and Drinking Water

F. Kozisek and I. Rosborg

The composition of water varies widely with local geological conditions. Both groundwater and surface waters begin as pure rainfall which is impacted by contact with the earthen minerals, reducing its purity. Thus fresh water contains certain amounts of gases, minerals and organic matter of natural origin. The total concentrations of substances dissolved in fresh water considered to be of good quality can be hundreds of mg/L (Aastrup et al. 1995).

The main function of drinking water is to provide hydration, but due to the presence of minerals, water can serve as a desirable source of essential elements. There are around 20 essential minerals for humans. The macro minerals are Ca, P, Na, K, Mg, Cl and S, needed in mg amounts every day, while Fe, Cu, Zn, Mn, Se, I, Mo and Co are micro minerals, needed in μg amounts. In addition, B, Li, Cr, Si, Ni, Sn and V are debated. F is needed for proper tooth enamel. Contribution of drinking water to total daily intake of these elements is often less than 10%, although in certain conditions it may represent up to 30% or even more (Rosborg and Nihlgård 2018). Nevertheless, even contributions lower than 10% may under some circumstances have a beneficial impact on health status, especially if intake of these elements from food is not sufficient and the organism is in borderline or manifest deficiency. This is known, for example, for Mg deficiency (Rubenowitz et al. 1999, Leurs et al. 2010), and the calcium uptake was significantly higher from mineral water in lactose-intolerant adults than in subjects drinking milk (Halpern et al. 1991).

Awareness of the importance of minerals and other beneficial constituents in drinking water has likely existed in some form for thousands of years, at least in some ancient civilizations, being mentioned in the Vedas of ancient India. In the book Rig Veda, the properties of good drinking water were described as follows: "Sheetham (cold to touch), Sushihi (clean), Sivam (should have nutritive value, requisite minerals and trace elements), Istham (transparent), Vimalam lahu Shadgunam (its acid base balance should be within normal limits)" (Sadgir and Vamanrao 2003).

Diseases connected to specific bedrock chemical compositions have been recognized in different parts of the world. Skeletal and dental remains of Native Americans from parts of Kentucky indicate mineral deficient soils and water, as cultivated maize had extremely low Mn and Zn levels (Moynahan 1979). In Norway farmers have been aware of unusual frequencies of osteomalacia, softening of bone tissue, among domestic animals in certain districts for hundreds of years. Originally, in medieval times, the farmers suspected a specific plant to cause the disease, "Gramen Ossifragum" (The grass that breaks bones) and they combated the disease with crushed bones added to the food of the animals (Voisin 1959). It was finally concluded that P was the deficient element. In Scandinavia and many other countries the importance of F for teeth (i.e. prevention of tooth decay) has been recognized since World War II. Contrary, negative impacts on teeth were noted on domestic cattle after an eruption of the Icelandic volcano Hekla. It was later determined that they suffered from dental fluorosis due to elevated F levels in soils and water after the eruption (Weinstein and Davison 2004). Due to transition from a hunter-gatherer society to an agriculturally based economy, Fe deficiency appeared among humans, as Fe from plants is more difficult to absorb than Fe from meat (Robertson and Manchester 1959). The Keshan disease, heart failure occurring especially in small children in some regions of China, is related to low Se concentrations in locally produced grains and drinking water (Yang et al. 1988). Selenium deficiency may also cause muscle degeneration in general in cattle and sheep (Hamliri et al. 1993), and some cancer frequencies appear to be lower in districts with elevated Se (Whanger 2004). Skin cancer and other pathologies due to As poisoning from drinking water is still a serious threat to hundreds of thousands of people living in regions with high As level in the drinking water (WHO 2017).

The first modern conceptions of nutritional importance of mineral elements in drinking water can be traced back to the period starting with the dawn of modern science in the nineteenth century. They appeared in relation to investigation of chemistry of medicinal (mineral) waters and to empirical observation of health impacts caused by some changes in water supply: "It can be considered as a very interesting fact in this way, that incidence of struma (goitre) in Vienna increased by 200% after building new supply piping mountain water in 1872" (Kabrhel 1927). Also, a note from UK was: "Some years ago the medical officer of the Eastern and Western Telegraph Companies consulted us respecting several of their stations in tropical climates where the only water available was the distillate from seawater. At these stations he had found that the teeth of their men were markedly affected, and he wished some simple process devised whereby a small but uniform quantity of calcium carbonate, $CaCO_3$, could be introduced into the water." (Suckling 1944).

Another source of knowledge on negative health effects of water with low mineralization were case histories from alpine climbing or polar expeditions which used melted snow as the only source of drinking water. The first such reports appeared in scientific literature in mid of the twentieth century (Schikina et al. 1984). The symptoms were derived from acute water and mineral imbalance and water intoxication, and include weakness, fatigue, convulsions, unconsciousness, and even death.

Most frequently investigated essential elements in water of the second half of the twentieth century were F, and Ca+Mg (or hardness). It is generally acknowledged that the research boom on health effects of water hardness was started with the paper of the Japanese chemist Kobayashi (1957) who demonstrated, based on epidemiological analysis, that higher mortality rates from stroke occurred in the areas where Japanese rivers, used for drinking purposes, contained higher levels of acidic water when compared to those with harder, more alkaline water. It can be documented that such observations are in fact much older and may be traced back before World War I (Thresh 1913) and even as far back as the 1870's when Dr. Letheby studied the relationships between total mortality and water hardness in 19 cities in England and Scotland (Anonymus 1871). As mortality rates differed widely, attempts to find the cause and differences in hardness of local water supplies seemed to provide a reasonable explanation. Most of these studies have shown that regular use of hard water is associated with significantly lower mortality due to cardiovascular diseases and also increased longevity.

1.3 Short History of Health Resorts, Wells with Different Mineral or Gas Contents, Expected Health Impacts

I. Rosborg and F. Kozisek

Healing effects of water have been recognized for thousands of years. Initially the focus was on the health effects when people were bathing in certain waters, mostly in thermal and sulphuric springs, but later they empirically recognized special effects of drinking waters, which had particular taste and mineral content (Bergmark 1959).

During the eighteenth and nineteenth centuries, the well off people in Europe went to numerous health resorts and spas to drink their special waters or take a bath in it. It was believed that the mineral content was important for cleaning the body by drinking a lot. Health resorts were often chosen to help a person with a certain

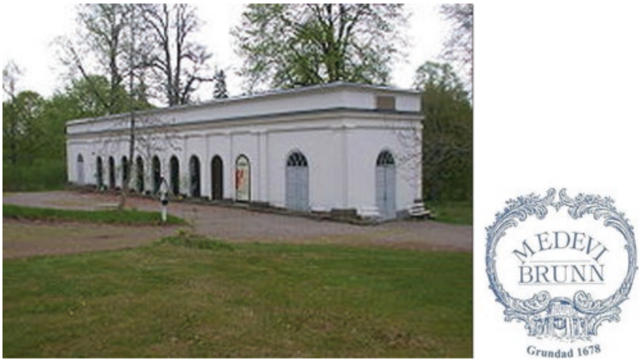

Fig. 1.2 Medevi Brunn, Sweden's oldest spa, established 1678, still popular (Photo: Göransdotter B)

complaint, as resorts were located at distinctive springs and there were claims of specialized effects for groups of diseases (Fig. 1.2).

Water with high concentrations of hydrogen carbonate, HCO_3, was known to neutralize acids, and to have a pain relieving effect on gastric ulcer, as well as alleviating acidosis. HCO_3 was also regarded as pain relieving on stomach pain itself, as it is transformed to carbonic acid, H_2CO_3, and carbon dioxide, CO_2, was emitted in the acidic environment in the stomach, thereby enlarging the volume of the stomach by the formed gas. In addition, water with HCO_3 was known to be expectorant, increasing digestion by making the intestinal mucus less viscous, as well as health bringing for people with gout and stones in the kidneys. It should be added that waters with high levels of HCO_3 were also high in TDS, Total Dissolved Solids, especially in Ca, so it is hard to differ what is "pure" effect of HCO_3 and what is effect of other dissolved solids or whole specific mixture. Table salt in water, NaCl, was known to be readily absorbed by the intestines and distributed into the body organs, and had an expectorant effect in all mucousa, by an osmotic effect on the mucous cells. This osmotic effect was called "the salt effect" in literature from this era. Salt water was also regarded protective against gout and cramps (Bergmark 1959).

Sodium sulphate, Na_2SO_4, and magnesium sulphate, $MgSO_4$, were not as easily absorbed in the intestines as NaCl, but tended to bind water in the intestines, and counteract constipation. In addition, water with elevated concentrations of Na_2SO_4 was considered to be of value for people with Pb poisoning, assuming it had a purging effect and also formed insoluble lead sulphate, $PbSO_4$, which then was conveyed by the faeces out of the body. Bitter salt, $MgSO_4$, was found to be relieving during attacks of biliary colic, as it made the gall bladder more easily emptied. Sulphur itself acted strengthening on the stomach and cleaned the spleen. Water pouring through soil containing gold, Au, was thought to be beneficial for eyes, against rupture and fistula (Bergmark 1959).

Especially people with anaemia visited wells with high concentrations of alkaline iron carbonate, $FeCO_3$, or, iron sulphate, $FeSO_4$. Some of these waters also had elevated arsenic, As, concentrations (Bergmark 1959, Hult 2007). Lithium is nowadays used as medication against depression, and was supplemented to water a hundred years ago. In some mineral wells in the Czech Republic there are Li-concentrations up to 3 mg/L. In some mineral wells in Spain and other countries there were waters high in As, copper (Cu) and radon (Rn) (Fig. 1.3). The health bringing effect of at least Rn and As are questioned today. However, spa Jachymov in the Czech Republic, as well as in spas Bad Gastein and Bad Kreuznach in Germany, still use water with high concentration of Rn for bath and the curative effect is well proven (Kozisek, oral comm., http://www.laznejachymov.cz/en/healing-sources/).

Arsenic rich water was used to cure leukaemia and anaemia (Hult 2007). Today, about 100 million people are suffering from poisoning due to high As in drinking water and they are potential candidates for skin cancer and a number of other diseases. The World Health Organisation, WHO (WHO 2017, WHO 2000), has declared As crisis as a public health emergency. However, the exposure to Rn or As rich water in health resorts was limited to only a few weeks per year, and no long term negative impacts on people who used it is known.

There are recipes on how to produce a health bringing drinking water from the eighteenth century. A Swedish recipe from 1765 states: Mix 52 g Fe filings with 104 g sulphur (S), leave it hanging in a towel in 5 L of water, add NaCl and drink every day. When a gall apple shifts colour the water needs regeneration. In addition, special powders were sold to be added to water to form mineral water (Hult 2007). Nevertheless, it is necessary to say that numerous attempts of the 19th and 20th

Fig. 1.3 Bottled Bornholm radioactive health water was labelled with the indication: "The water is guaranteed good for gout, nervousness, fatigue, anaemia, metabolic disorders, and decrepitude" (Jönsson 2014)

centuries to produce artificially waters with the same reported curative properties as natural medicinal waters (such as Carlsbad water) were not successful (Krizek 1987).

Nowadays, balneology, the study of therapeutic benefits from intake of mineral water, hot baths or bath in water naturally rich in CO_2 (which may improve blood perfusion of limbs and blood circulation) are part of the general medicine especially in parts of Central and Eastern Europe and Japan. By drinking special mineral waters and bathing in hot or carbonated springs the patients may be healed or symptoms substantially reduced and mitigated. Some procedures based on drinking special mineral waters were proved to be efficient in treatment of certain diseases by modern scientific methods and they have no undesirable side effects (like the side effects from treatment with some pharmaceuticals). However, these remedies are less and less prescribed and used today, because they require at least 3–4 weeks of application (stay at the resort), which is less and less accepted in our modern restless society. In Western Europe, water therapy is almost completely denied as a healing process, but traditional health resorts are still used at least for regeneration after hospital treatment or just for relaxation and wellness stays (Karagülle 2012).

1.4 Elements in Bedrock and the Influence on Water

O. Selinus

1.4.1 The Bedrock

The main natural source of elements in groundwater is the bedrock (and soils derived from the underlying bedrock). Therefore it is important to have knowledge of the elemental content of different bedrock types. This is not easy because the variation is huge even within the same type of bedrock. There is a separate science dealing with this, geochemistry, and one basic task of geochemistry is how to sample the bedrock to get representative analyses, which is often quite complicated. The terms minerals and elements are used in slightly different ways in nutrition and geoscience/chemistry. In the latter case minerals mean a naturally occurring compound with definite chemical composition and crystalline structure, of which there exist over 4000 officially defined species, examples being quartz, feldspar, mica etc. The term elements are used as the elements in the periodic system, for example Cu, As, Au, etc. In nutrition, minerals may be the same things as elements in geosciences, meaning the elements in the periodic system. These variations could be confusing when comparing nutrition and geoscience. Microelements in nutrition are trace elements in geoscience. In this brief overview we use the geoscientific terminology. Minerals are for example quartz and feldspar, while elements are those in the periodic table. The bedrock may be composed of various elements from region to region.

There are three major groups of bedrock: sedimentary, metamorphic, and igneous, each made of different sets of minerals and having quite different chemical composition of importance for the contents in groundwater. Igneous rocks form from cooling volcanic magma and lava. Examples are granites, basic rocks, and ultrabasic rocks. Metamorphic rock forms when pre-existing rocks, exposed to heat and pressure, change chemically. The heat and pressure cause some, but not all, of their chemical bonds to break and re-form. In this manner the old igneous or sedimentary rock becomes a new metamorphosed rock, examples are gneisses. Sedimentary rock is formed when accumulated pieces of broken rock, plant, and animal materials, which are carried by wind and water, settle and compact over millions of years into cemented layers. Examples are shales, greywackes, and limestones. These three different rock types have very different chemical compositions but if one knows which types are present in different bedrock types, it is possible to estimate which elements may be present in the resulting soils and groundwater (Meriam 2004, Garrett 2000, 2013).

These three different rock types have very different chemical compositions but if one knows which types are present in different regions it is possible to know approximately what elements could be present in soils and water. Table 1.1 shows concentrations of some selected elements in abundant rock species. It is important

Table 1.1 Concentrations of some selected elements in abundant rock species (values in mg/kg) (Meriam 2004, Thornton 1983)

	Mg	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se
Shales	16000	4600	130	90	850	48000	19	68	45	95	10	0.5
Greywackes	13000	3800	98	88	750	38000	15	24	24	76	8	0.1
Limestones	26000	400	20	11	700	15000	2	15	4	23	2.5	0.19
Granitic rocks	6000	3000	94	12	325	20000	4	7	13	50	1.5	0.04
Gneisses	13000	3870	60	76	600	33000	13	26	23	65	4.3	0.08
Basaltic and gabbroic rocks	37000	9700	251	168	1390	86000	48	134	90	100	1.5	0.09
Continental crust	22000	4010	98	126	716	43000	24	56	25	65	3.1	0.12
Ocean crust	45000	9700	252	117	1200	70000	45	144	81	78	1.5	0.17

	Mo	Ag	Cd	Sn	Au	Hg	Tl	Pb	U	Bi	F	I	Li
Shales	1.3	0.07	0.13	2.5	0.0025	0.45	0.68	22	50–250	0.11	740	2.2	60
Greywackes	0.7	0.1	0.09	3	0.003	0.11	0.20	14		0.07			
Limestones	0.4	0.0	0.16	0	0.002	0.03	0.05	5		0.02	330	1.2	20
Granitic rocks	1.8	0.12	0.09	3.5	0.0024	0.03	1.1	32	4	0.19	735	0.5	30
Gneisses	1.5	0.08	0.10	2.5	0.003	0.02	0.65	16		0.10			
Basaltic and gabbroic rocks	1	0.11	0.10	1.5	0.004	0.02	0.08	3.5		0.04	400	0.5	10
Continental crust	1.1	0.07	0.10	2.3	0.0025	0.04	0.49	15	2.8	0.08	625	0.5	20
Ocean crust	1.8	0.03	0.13	1.4	0.002	0.02	0.013	0.50		0.006			

to realize that a table like this only gives general information on the contents in bedrock and how they reflect the contents in soils and water. (Meriam 2004, Garrett 2000, 2013).

1.4.2 *Weathering*

Elements in bedrock must in some way be redistributed to be introduced in soils and groundwater. The redistribution of elements from bedrock into the surface environment, including water, occurs as a result of physical and chemical weathering that transforms rock, which is hard, non-porous and of low reactivity, to soil which is soft, porous and chemically active. Physical weathering breaks the rock into smaller particles, thereby increasing the surface area that is exposed to air, water, and often ice, which are the main agents of chemical weathering. The resistance of minerals to weathering depends partly on their mineralogy and partly on their chemistry. Most minerals are soluble to some degree under conditions existing at the surface. Some, such as calcite, dissolve readily, whereas others, including the most abundant aluminosilicates, are only partially soluble. Igneous rocks are easily eroded and chemically altered. Selected chemical associations of minor and trace elements in some types of rocks are given in Table 1.2. This table shows the association between elements in certain bedrock types. If for example high contents of molybdenum (Mo) appear in an area with granitic rocks there is also a possibility that uranium (U) is present in the water. Certain bedrock types are more susceptible for weathering, for example limestones and greenstones (basic and basaltic rocks). The latter bedrock type, as can be seen in Table 1.1 contains higher contents of several important elements as vanadium (V), chromium (Cr), nickel (Ni) etc. Some of these are important nutrients. Therefore, weathering of these rock types can release many more elements than more resistant rocks can, such as granites.

Table 1.2 Selected associations of elements (Thornton 1983)

Rock type or occurrence	Association
Plutonic associations	
Ultrabasic rocks	Cr – Co – Ni – Cu – Fe- Mg – Ca
Basic rocks	Ti – V – Sc – Fe – Mn – Ca
Granite rocks	Ba – Li – W – Mo – Sn – Zr – Hf – U – Th, Ti – F – K – Na
	Ti – F – K – Na
Hydrothermal sulphide ores	Cu – Pb – Zn – Mo – Au – Ag – As – Hg – Sb – Se – Te – Co – Ni – U – V – Bi – Cd
Sedimentary associations	
Black shales	U – Cu – Pb – Zn – Cd – Ag – Au – V – Mo – Ni – As – Bi – Sb
Elements with similar geochemistry	K-Rb; Rb-Cs; Al-Ga; Si-Ge; Zr-Hf; Nb-Ta; RE; S-Se; Br-I; Zn-Cd; Rb-Tl; Pt-Pd-Rh-Ru-Os-Ir

1.4.3 Selected Elements in Bedrock of Importance for Groundwater

1.4.3.1 Arsenic (As)

Arsenic is an element that occurs naturally in bedrock and in inorganic form in minerals. Soil and bedrock may have levels of 1–40 mg/kg. Lead (Pb), Cu and gold (Au) ores can contain up to 3% As. Moderate occurrence of As can be seen in acidic volcanic rocks and a high content of As is found in sulphide ores and black shales. Arsenic is a trace element present in many magmatic types of bedrock, in granites, in basic bedrock, and also in certain sedimentary bedrock types, especially in shales with high organic contents.

Arsenic is an increasingly important element. It can be found in high contents all over the globe. The most well known high levels are in Bangladesh and West Bengal. However, more and more reports come from many other countries. It is important to realize that if high contents are detected in a well, this does not mean that a well nearby also has high contents, only that the risk is higher in that region for As to be present. Arsenic is a typical example of the great variability of elements in bedrock. It should also be stressed that even if the As content is low it can be concentrated to much higher levels both through oxidation and reduction (Smedley and Kinniburgh 2002).

1.4.3.2 Fluoride (F)

Fluoride is highly mobile in water and most of it is in the oceans. Much F is bound in minerals and found in acidic volcanic rocks, mineralized dykes and sedimentary rocks. Fluoride is present in primary minerals, especially biotites and amphiboles, replacing hydroxyl groups. At weathering F tends to be redistributed. If biotites and amphiboles are abundant, such as in granite, these represent a major source of F in water. Limestones can contain high concentrations of fluorapatite. Most sandstones contain very low levels, and thus groundwater in those areas have low concentrations of F (Edmunds and Smedley 2013).

1.4.3.3 Cadmium (Cd)

Cadmium is found mainly in sulfide ores and is often associated with Zn. But also certain other rock types may have elevated contents such as some sedimentary bedrocks. It is more easily weathered from minerals if the soils get acidified.

1.4.3.4 Uranium (U)

Uranium can be found in several types of bedrock. Granites, shales and certain types of sandstones can contain quite high levels of U. In Sweden for example, with many granitic rocks, U in groundwater could in general be high and also reflected in the population.

1.4.3.5 Copper (Cu), Zinc (Zn), Lead (Pb)

Copper is often associated with sulfur in bedrock. The most common ores are chalcopyrite $CuFeS_2$ and bornite Cu_5FeS_4. Solid Cu occurs in veins that cut through sandstone. These veins of Cu frequently contain small amounts of Ag, Sb and Pb. The crustal content of Zn is relatively low and equal to that of Ni. To some extent Zn substitutes or replaces Fe and Mg in the mineral lattices. The main mineral of Zn is ZnS, sphalerite, which often occurs along with other sulphide minerals. Soils derived from basic igneous rocks have high Zn levels, while soils that come from more silica-rich soils are remarkably Zn poor.

The mobility of Pb in soil is one of the lowest of all heavy metals, generally resulting in low Pb concentrations in the groundwater. The mobility of Pb is pH-dependent and decreases significantly with liming and increased pH. Accumulation of Pb in surface soil layers is of great ecological importance, because it affects the biological activity in soil (Kabata Pendias and Mukherjee 2007).

1.4.3.6 Chromium (Cr)

Chromium does not occur in elemental form. The main mineral is chromite. Chromium is widespread. Basaltic rocks and "greenstones" normally have higher Cr content. Chromium occurs in several different oxidation states. The hexavalent compounds are the most toxic. Trivalent chromium is essential to normal carbohydrate, lipid, and protein metabolism. In contrast, chromium (VI) can induce carcinogenesis because of its ability to cross biological membranes easily and react with protein components and nucleic acids inside the cell (Sun and Liang 2008). Typical Cr(VI) containing waters have a $pH > 7.5$ and Ca concentration < 50 mg/L. Contact with ultramafic rocks activates Cr(VI) formation by a catalytic mechanism. Highest Cr(VI) values are observed in shallow porous aquifers downstream of ophiolites (Kaprara et al. 2015).

1.4.3.7 Selenium (Se)

Selenium has a low average concentration in the crust. It occurs both with sulfur in elemental form and in sulfidic ores. Selenium is as rare as Ag and Hg and more than 5000 times rarer than S. Pure Se minerals are rare. Volcanic rocks can contain more than 10 g of Se per ton. Selenium is also found in higher concentrations in some coal and petroleum deposits. In the oceans the Se concentrations are between 20 and 200 mg/ton which can be seen along the coasts where the Se contents in the environment is high because of sea spray (Fordyce 2013).

1.4.4 Where to Find More Data?

The contents of elements in bedrock and soils have an enormous influence on the contents of mineral elements in water. Can these be mapped and are there any databases which can be used? This knowledge is important because it is needed to link this data to the impacts on human health (Selinus et al. 2013, Reimann and de Caritat 1998).

The International Geochemical Mapping Project, the main aim of which was to establish standards, was accepted in 1988. Plans for a Global Geochemical Mapping Project using wide-spaced sampling were then accepted as the project entitled "Global Geochemical Baselines" in 1995. As one step the compilation of the "Geochemical Atlas of Europe" was carried out by the Geological Surveys of the European Union. The European survey covered 26 countries and provided information in different sample media of the near-surface environment (topsoil, subsoil, humus, stream sediment, stream water, and floodplain sediment). This was the first multinational project, performed with harmonized sampling, sample preparation, and analytical methodology, producing high-quality compatible data sets across national borders. Over 60 determinands (as indicators) were established, 400 maps plotted and interpreted, most for total and aqua regia-extractable concentrations. The entire database can be downloaded free of charge (Salminen et al. 2005). All maps can also be downloaded from the web (Fig. 1.4).

Also a new comprehensive guide to European groundwater prepared on the basis of analyses of bottled water has been carried out (Reimann and Birke 2010). The new atlas provides the chemical composition of 1785 bottled water samples from 38 European countries. The survey is important, since more than 1900 brands of bottled water are currently registered in Europe and the market is rapidly expanding. Some bottled water samples exceeded the drinking water standards for parameters, such as, As, Ba, F, NO_3, NO_2 and Se. The range in concentration of chemical elements in bottled water represents the range naturally found in European groundwater, which also to a high extent reflects the native bedrock, except for RO treated or Na/K salt supplemented bottled waters.

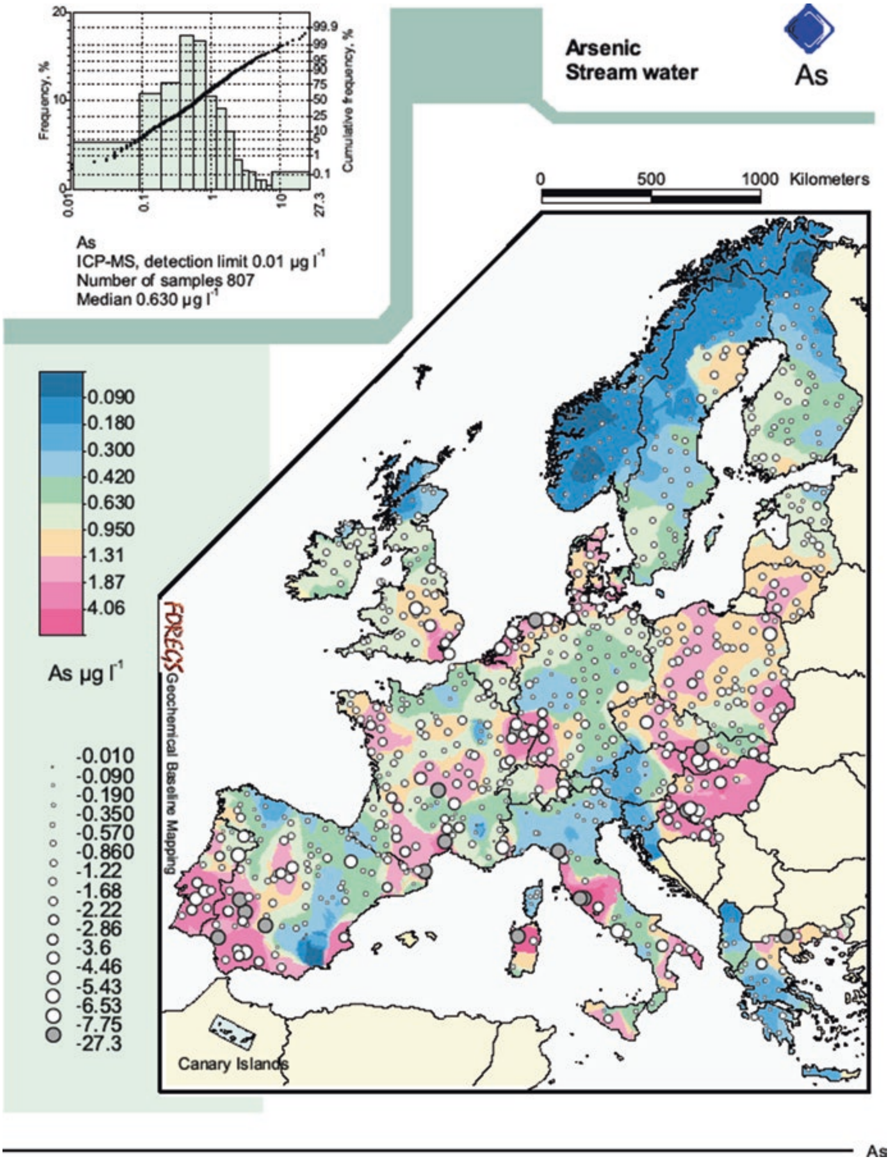

Fig. 1.4 Arsenic (As) in surface water in Europe. An example of a continental quality controlled survey of elements in surface/groundwater (Salminen et al. 2005)

1.5 Minerals and Mineral Ratios in the Human Body

M. Ferrante, I. Rosborg, and F. Kozisek

The abundance of the minerals in the human body is approximately 5% of the body mass. Mineral elements required at a dose bigger than 100 mg per day are considered macro elements, such as Ca, Mg, K, Na, Cl, S and P. Others such as Zn, Fe, Cu, Mn, I, Mo, Co and Se are known as micro or trace elements. Boron (B), Li, Cr and V are other potentially essential elements. The largest amount of the total body minerals, Ca and P, in a "reference man" is osseous (bone) minerals, and other elements such as K, Na and Cl are primary extraosseous minerals (Wang et al. 1992).

The serum Ca concentration in the human body is 2.4 mmol/L, normally ranged 2.2–2.5 mmol/L (8.8–10.4 mg/dL) (Table 1.3). This narrow range is mainly under the long-term control of the parathyroid hormone and vitamin D. The physiologically relevant form, important for most functions of Ca in human body, is the free Ca ion, which makes up 50% of the total serum Ca level (Peacock 2010). However, promptly after an approximately 10% increase in the serum Ca level (such as, 1 h after a Ca rich meal) secretion of calcitonin (hormone of thyroid gland) is increased and returns Ca to the physiological range. The rapid buffer exchangeable pool of Ca-salts in bones plays the most important role in plasma Ca regulation (Pirklbauer and Mayer 2011).

A human adult body contains about 24 g of Mg (Herroeder et al. 2011), although its concentration in serum is relatively low ranged 0.7–1.15 mmol/L (1.8–2.8 mg/dL) (Bourre 2006). Other sources give a slightly higher level 3.7–4.9 mg/dL (Bloodbook 2013). Mg is stored mainly in bone tissue (60%) and the intracellular compartments of the muscles (20%) and soft tissues (20%), primarily bound to chelators, such as adenosine 5′-triphosphate and DNA (Herroeder et al. 2011). Mg homeostasis is maintained as a balance between intestinal Mg absorption and renal Mg excretion. If the serum Mg level is raised the Mg urinary excretion is also raised and vice versa (Cole and Quamme 2000).

The serum K level is 3.8 mEq/L (normal 3.5–5.5 mEq/L, 13.7–21.5 mg/dL). Urinary K excretion reflects dietary K intake. After 18 days on high K diet, urinary K excretion increased from 2.0 to 9.1 g/day (50–233 mmol/day). The level of Na intake does not appear to influence K excretion except at levels of Na intake above 6.9 g, at which point net loss of K has been demonstrated. The normal human kidney efficiently excretes K when dietary intake is high enough to increase the serum concentration even slightly, but inefficiently conserves K when the dietary intake and thus the serum concentration is reduced (FNB 2005).

Na and Cl appear together in most food as NaCl, and are also responsible for maintaining the extracellular volume and plasma osmolality. The minimal amount of Na required to replace losses is estimated to be about 0.18 g (8 mmol/day) (FNB 2005).

Eightyfive percent of the body P in an adult is in bone tissue, and the remaining 15% is distributed through the soft tissues. Average total amount of serum inorganic

Table 1.3 Mineral content of normal human blood serum and the whole body; recommended daily intake (Peacock 2010, Bloodbook 2013, FNB 2005, Abramowitz et al. 2012, Bowman and Russell 2006, NFAS 2018, Deng et al. 2008, Wallach 2007)

Mineral	Normal concentration ranges in serum	Total content in the whole human body	Recommended daily intake, adult 70 kg, approximate value
Calcium	8.8–10.4 mg/dL (9.4)	1000–1200 g	1000 mg
Magnesium	3.7–4.9 mg/dL (4.3)	25–30 g	300 (420) mg
Hydrogen carbonate	110–140 mg/dL (125)		
Sulphate	27–30 mg/dL		
Sodium	311–335 mg/dL (323)	90–100 g	< 2 g (min. Required 0.18 g)
Potassium	13.7–19.6 mg/dL (16.7)	140–225 g	3 g
Phosphorous	3.0–4.5 mg/dL (3.75)	750–850 g	700 mg
Chloride	350–376 mg/dL (363)	82 g	< 3 g
Iron		2.1–2.8 g	12 mg
Copper	70–150 µg/dL (110)	70–80 mg	0.8 mg
Mo			45 µg
Zinc	0.06–0.12 mg/dL	1.5–2.5 g	8 mg
Chromium	5–55 µg /dL (30)	6 mg	100 µg
pH	7.34–7.45		
Ca/Mg	2.1–3.1:1		3:1
Na/Ca	32–35:1		2:1
Na/K	20–40:1		0.67:1
Ca/P	2.3–8.5:1		1.4:1
Na/Mg	68–84:1		0.6 (min)–7:1
(Na + K)-(Cl + HCO3)	3.0–11:1		

P in both forms (HPO_4^{2-} and $H_2PO_4^-$) is 1.3 mmol/L, normally ranged from 1.1 to 1.3 mmol/L (3.3–4.0 mg P/dL). Excretion of endogenous P is mainly through the kidneys (FNB 2005).

The serum or plasma HCO_3 is part of the homeostatic mechanisms for maintaining the acid-base balance in the blood. Serum HCO_3 levels have been shown to decrease in a linear fashion with increasing acid loads. Together with K, Na and Cl, serum HCO_3 is used for calculation of anions gap (difference in measured cations and anions: ($[Na^+] + [K^+]$)-($[Cl^-] + [HCO_3^-]$)). Levels of anion gap of 3–11 are regarded normal, while levels >11 is high. Metabolic acidosis is connected with high anion gap. Lower levels of serum HCO_3 and a higher anion gap have been associated with insulin resistance, hypertension in the general population and lower cardiorespiratory fitness in adults (Abramowitz et al. 2012).

Absorption of SO_4 from the intestine depends upon the amount of SO_4 ingested, and the type of cation associated with SO_4. Associated with Mg, SO_4 is absorbed to a lesser extent than bounded with Na. Most SO_4 found in human tissues is biosynthetically incorporated into macromolecules and is organic (such as, muccopolysaccharides, chondroitin sulphate, glycolipids, steroids, thyroid hormones). Inorganic SO_4 represents a small fraction of the total SO_4 in the body. The normal serum level of inorganic SO_4 found in humans is 0.3 mmol/L or 2.9 mg/dL. Infants and young children have higher serum inorganic SO_4 concentration than adults (4.5 mg/dL). Ingesting drinking water containing high SO_4 concentrations has only slight effects on serum SO_4 levels. Thus, a 15 fold increase in SO_4 concentration in drinking water will result in only a 1.4 fold increase in serum SO_4. The reasons could be homoeostatic control mechanisms and dietary differences. Elimination of SO_4 occurs through urinary excretion (US EPA 2003).

Since the plasma concentrations of the electrolytes (K, HCO_3, Na, and Cl) are highly regulated, their plasma concentrations remain normal or little changed despite substantial increases in their dietary intake. This compartment serves as primary source from which the cells of all tissues take all necessary elements for their proper functioning. However, serum levels of minerals are not sensitive indicators of their adequate intake related to preventing chronic disease (FNB 2005).

As shown in Table 1.3 the dominant serum cation and anion in the human body is Na and Cl, respectively, which are responsible for the maintenance of an adequate osmolarity of the extracellular fluid. This results in high molar ratios of Na and Cl to the other cations and anions. In contrast, the molar ratios of the electrolytes in the intracellular fluid are completely different, since the main intracellular cation and anion are K and PO_4, respectively. An optimum mineral ratio for the main mineral constituents that the body requires on a daily bases is influenced by factors such as age, absolute quantities of each element, bioavailability and physiological adaptive responses. Thus, it is very difficult to determine the optimum mineral ratios. For example, if growth were the only consideration, the intake ratio of Ca/P would have to be substantially higher than 2:1 after infancy, because the Ca absorption drops more sharply with age than does the phosphorus absorption. Furthermore, in balance studies of human adults, Ca/P molar ratios ranging from 0.08:1 to 2.40:1 (a 30-fold range) had no effect on either the Ca balance or the Ca absorption (IOM 1997).

People worldwide are facing mineral deficiencies, despite the increasing caloric intake. Diets based on processed foods are high in Na and low in K (Adrogue and Madias 2007). This was confirmed by a large epidemiological study (SU.VI.MAX) carried out in France, showing that a large fraction of the French population ingest less than 2/3 of the amounts proposed for vitamins and minerals in the recommended nutritional intakes (Bourre 2006). If a daily energy need of 2100 kcal is satisfied by plant materials (2/3 of energy) and animal food (1/3 of energy) (considered as a “Natural diet”) the daily intake of Na is approximately 500 mg, that of K about 7400 mg, Ca approximately 1100 mg, and Mg about 800 mg. In “Modern diets”, intake of Na was six-fold higher, intake of Mg approximately 180 mg, and intake of Ca approximately 40% of the amount provided by the Natural Diet

(Karppanen et al. 2005). High urinary Na excretion (approximately 9.9 g of NaCl per day) was shown in the large International Study of Salt and Blood Pressure (INTERSALT), which included participants from 32 countries (ICRG 1988). Sacks et al. (2001) found that reduction in Na intake caused stepwise decreases in blood pressure, and population studies have shown an inverse relation of K intake to blood pressure, the prevalence of hypertension, or the risk of stroke. The urinary K/Na ratio in the INTERSALT study had a significant inverse relation with blood pressure. This ratio bore a stronger statistical relationship to blood pressure than did either the Na or the K excretion alone (Adrogue and Madias 2007). In one study a 50 mmol (2.0 g) higher excretion of urinary K was associated with a 2.5 and 1.5 mm Hg lower level of systolic and diastolic blood pressure, respectively (Rose et al. 1988). K restriction causes a deficit in cellular K that triggers cells to gain Na in order to maintain their tonicity and volume. Na retention and K deficit may alter the Na pump of the arterial and the arteriolar vascular smooth-muscle cells and lead to increased Na concentration and decreased K concentration in the intracellular fluid. Increased intracellular Na stimulates the Na–Ca exchanger in the membrane, driving Ca into cells. Further, K channels in the cell are inhibited with the deficit of K in the body leading to membrane depolarization and further rise in intracellular Ca. The increased cytosolic Ca caused by these mechanisms triggers contraction of the vascular smooth muscle and increasing blood pressure (Adrogue and Madias 2007). The Western diet gives rise not only to low-grade K deficiency, but also to low-grade HCO_3 deficiency (expressed as metabolic acidosis) (FNB 2005). Large genome-wide association study of serum Mg, K and Na levels in 15,366 community dwelling subjects of European ancestry from the Cohorts for Heart and Aging Research in Genomic Epidemiology Consortium (CHARGE) discovered common genetic variants in six genomic regions that were significantly and reproducibly associated with the serum Mg levels and clinically defined hypomagnesemia. Associations with serum K and Na did not reach the level of genome-wide significance in this study. This study also provides evidence for a role of the encoded Mg transporters in the regulation of the physiological Mg homeostasis in humans (Meyer et al. 2010). In the case of mineral deficiencies, especially the Mg and K composition of drinking water may play an important preventive role for cardiovascular diseases, primarily. If water is high in some other macro or micro constituent the drinking water may be considered to be an important source of essential mineral.

1.6 Osmotic and pH Balance in the Human Body

D. Jovanovic, I. Rosborg, and M. Ferrante

Water and its mineral constituents are dynamically linked in the human body. The amounts of these minerals in healthy people remain constant or within relatively narrow ranges, due to the biological balance between intake and excretion and various homeostatic mechanisms. As the most abundant component of the human body,

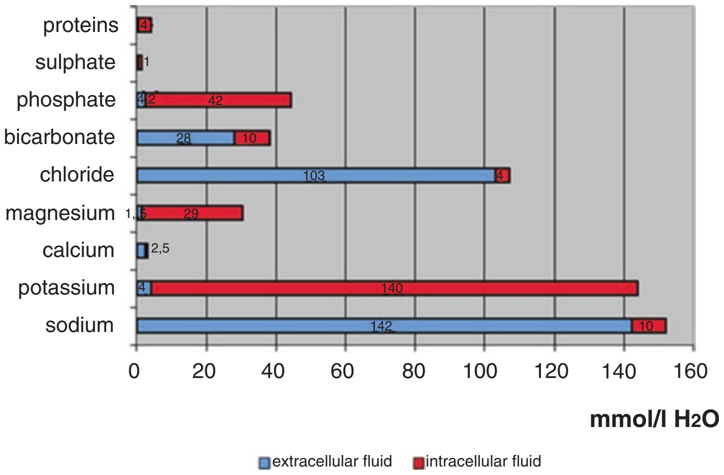

Fig. 1.5 Concentrations of osmotic active substances in extracellular and intracellular fluids

water makes up approximately 60% of the body weight distributed intracellularly (40%) and extracellularly (20%). The water amount in the body depends on age, gender and body fat (decreases with age and total body mass in obesity). The osmolarity of the body fluids mostly depend on the concentrations of univalent electrolytes such as Na, Cl and HCO_3 in the extracellular and K and PO_4 in the intracellular space (Fig. 1.5) (Pecelj-Gec 2002).

Adequate regulation of the volume and osmolarity of the extracellular fluid (ECF), through maintaining salt and water balance, is very important to maintain the blood pressure and prevent swelling or shrinking of cells. Expansion or reduction in the ECF volume, respectively, causes a rise or fall in the arterial blood pressure. The kidneys and the thirst mechanism have the main roles in this regulation. One more important part of the human homeostasis is the acid-base balance, which is tightly regulated in a narrow pH range, between 7.35 and 7.45. In the state of acidosis or alkalosis, even small pH changes alter the neuromuscular excitability and enzyme activity, among other serious consequences. Three mechanisms are involved in maintaining a normal pH level in the human blood: renal, respiratory and chemical buffer systems in the body fluids (HCO_3, Ca, PO_4, proteins and haemoglobin buffer systems) (Tortora and Grabowski 1996). Cell culture experiments show that a decrease in extracellular pH (acidosis) has an inhibitory effect on the activity of cultured osteoblasts and alkaline phosphatase, both involved in mineralization of bone matrix. Contrary, cultured osteoclasts (responsible for bone resorption) are stimulated directly by acidity via H^+-sensing ion channels (Arnett 2008), which is the reason that acidosis has a negative impact on the skeleton and indirect influence on the mineral content in the body.

In healthy elderly persons net endogenous acid production, measured as net acid excretion (NAE), is in close relation to excretion of both Mg and Ca (Rylander et al.

2006). In a meta-analysis of 25 studies major variations were shown in the excretion of Ca based on whether the urine was acidic (might be as low as 5) or alkaline (may be above 8). With each milli-equivalent change of NAE the change of the Ca excretion was 0.035 mmol/day for acid, and 0.023 mmol/day for alkaline urine. Given that the estimated average quantity of NAE of the modern diet was 47 mEq/day the excreted amount of Ca was 1.6 mmol/day (66 mg/day) (Fenton et al. 2008).

Modern western diet is characterized by an increased intake of animal food and cereal grains (Vormann and Remer 2008), high salt and low K intake (Frassetto et al. 2008). In contrast, diets of our ancestors (pre-agricultural societies) were net base-producing with higher ratios of plant-to-animal source food in the diet (Sebastian et al. 2002, Strohle et al. 2010). Aside from acid or alkaline-yield diet, drinking water or choice of mineral water may also have an influence on the acid-base metabolism and mineral homeostasis.

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Chapter 2
Mineral Composition of Drinking Water and Daily Uptake

Bengt Nihlgård, Ingegerd Rosborg, and Margherita Ferrante

Abstract Conductivity gives a rough idea of the amount of dissolved ions in water (mS/m) or (µS/cm). Distilled water is <1 µS/cm, Reverse Osmosis treated 1–10 µS/cm, water from some sorts of sandstone or from granite (soft water) 5–15 µS/cm, and water from limestone (hard water) 20–200 µS/cm. Thus, the variation of the contribution of minerals from drinking water is large. A Swedish study on well waters, bottled waters and municipal waters showed the following contributions to the daily intake (2 L consumption): Ca 0–72%, Mg 0–69%, Na 0–65%, Cu 0–250%, Fe 0–46%, without considering that minerals in water generally are more readily absorbed in the intestines than minerals from food. Some springs and bottled waters with elevated concentrations of especially Ca, Mg and HCO_3 may be regarded medical waters and used by people suffering from acidosis and subsequent diseases.

2.1 The Conductivity Reflects the Ionic Content, Minerals and Toxic Ions of Water

Bengt Nihlgård

Broadly the contents in drinking water are inorganic ions, gases, organic impurities, bacteria, suspended matter and sometimes radioactive isotopes of elements. The last four types of contaminants, however, are normally controlled or eliminated by various methods available for treatment (WHO 2005). Inorganic salts and organic

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Table 2.1 Values on the specific ion molar conductance for some ions (CRC Handboook 1999)

Specific ion molar conductance, λ (in water, 25 °C)			
Cations	*(mS/m/mol)*	Anions	*(mS/m/mol)*
H^+	34.97	OH^-	19.8
Na^+	5.01	Cl^-	7.63
$1/2Ca^{2+}$	5.95	$1/2CO_3^{2-}$	6.93
$1/2Fe^{2+}$	5.4	HCO_3^-	4.45
$1/3Fe^{3+}$	6.8	$1/2HPO_4^{2-}$	3.3
K^+	7.35	$H_2PO_4^-$	3.3
$1/2Mg^{2+}$	5.3	$1/2SO_4^{2-}$	8.0
$1/2Mn^{2+}$	5.35	HSO_3^-	5.0
$1/2Zn^{2+}$	5.28	HSO_4^-	5.0
NH_4^+	7.35	NO_3^-	7.14
Li^+	3.87	$1/3PO_4^{3-}$	6.9

elements usually originate from the soils, but today also from manmade contamination and industrial sources. Principally, however, the chemical composition of bedrocks and soils and dissolved organic matter from the soils will determine the chemical composition of the water passing through.

Chemical or photometric methods are used to quantitatively analyse the major 15 minerals in water, and about 55 other elements have been found in trace amounts, detectable by sensitive methods like ICP-MS or similar (Rosborg et al. 2005). An absolute majority of the elements appear as dissolved ions in the water. To get a quick idea of the amounts of dissolved ions, the conductivity in millisiemens per meter (mS/m) or microsiemens per cm (µS/cm) is measured. This electrical conductivity (EC) is measured between two metal plates, and it is a simple, but very cheap, robust and informative measurement. Conductivity is only slightly dependent on temperature, but it's recommended to measure it in water warmed up to 20–22 °C (Nihlgård 2008), or to use a temperature compensating conductivity meter. Conductivity informs us about the relative content of total dissolved solids (TDS), dominated by salts dissolved as ions with their specific electrical charges. Obviously, conductivity does not provide any information on the concentration of any single element and composition of TDS.

Each element ion has a specific ion conductivity, and the contribution to the total conductivity in the solution thus depend on the concentration of each element. Specific ion conductance of some common ions in drinking water are presented in Table 2.1.

H^+ and OH^- have the highest ion conductance values, depending on electron mobility for these ions, while other ion conductance values primarily depend on the size of the ions in water solution. Based on the specific ion conductance values and knowledge of ion concentrations it's then possible to roughly recalculate the electrical conductivity (EC) of a solution (Brett and Brett 1993), by summing up all ions specific conductivities:

$EC = \Sigma \lambda_{c,}.c_{i.}$ (where $\lambda_{c,i}$ is the specific ion molar conductance, and c_i the molar concentration of each ion).

Table 2.2 Common ranges of different conductivity-values and pH-values in natural waters

	Conductivity range		
Type of water solution	µS/cm	mS/m	pH range
Distilled water	<1	<0.1	5.6–6
Rain water in clean areas	<1–5	<0.1–0.5	5.6–7
Rain water in industrial areas	10–30	1–3	4–9
Mountain brook water, sandstone	5–15	0.5–1.5	5.6–6
Mountain brook water, limestone	20–200	2–20	6.5–8.5
Oligitrophic (mineral poor) water	30–100	3–10	5.5–8
Mesotrophic water	100–250	10–25	6–8
Eutrophic (mineral rich) water	250–600	25–60	7–9
Sea water (salinity 3–3.5%)	40000–50000	4000–5000	8–8.2
RO (reverse osmosis) treated water	1–10	0.1–1	6–8

Common ranges of different conductivity-values (µS/cm) in natural waters, in combination with pH-ranges, and in comparison with distilled and reverse osmosis water are presented in Table 2.2.

It is obvious that rainwater in clean areas is practically distilled water, with conductivity values usually close to 1.0 µS/cm, and pH has stabilized itself in balance with carbon dioxide in the air to form a certain amount of carbonic acid, which lowers the pH to approximately 5.6. Similar conductivity is found in reverse osmosis treated water (RO), if no carbonic acid is added to decrease the pH to enable re-mineralization.

We can roughly assess the value of Total Dissolved Solids (TDS) from the value of conductivity. TDS (in mg/L) is usually 7–9 times higher than the value of conductivity (in mS/m) (Pitter 2015).

Depending on whether basic minerals or natural organic matter (humic acids) is added to the water passing through the soil, the pH-value can increase up to 8.5 or decrease even below 4.5 (Nihlgård 2009). Most waters recommended as drinking water and with suitable concentrations of salts, but without extra added carbonic acid, have conductivity values from 150 to 300 µS/cm (i.e. 15–30 mS/m) (Fig. 2.1).

2.2 Drinking Water as a Source of Minerals

I. Rosborg and M. Ferrante

Individuals who would receive the greatest benefit from the presence of minerals in drinking water are those with deficient or marginal intakes from their food sources. Ca, Mg, Se, Mo, Cr, F, I, Zn, Na, K, Cd, Si and other minerals may be present in drinking water, since they are present in soils and the bedrock (Rosborg 2005).

Fig. 2.1 Quarries in Cambrian sandstone (SGU 2014). Water from sandstone bedrock is generally low in minerals, but there are exceptions, as some kinds of sandstone have limestone as the glue between sand grains

Absorption of minerals from drinking water is determined by several factors. Se (selenite, selenate) may be somewhat less absorbed from water than from food containing seleno-aminoacids. Cu and Zn are less absorbed in elderly people, and Fe, Zn, Cu, Mn and Cr are absorbed to a higher extent in deficiency. Se-I, Cu-Fe are pair wise dependent on the presence of the other nutrient for metabolism. The bioavailability of Ca, Fe, Mg, P, Cu or Zn is depressed by foods/diets high in phytate, as cereals. Phosphorus and triglycerides bind to Ca, and may reduce the absorption of Ca. Sulphides can bind Cu, and other heavy metals. Minerals that share transporters can be mutually inhibitory; SO_3-SeO_3, Ca-Zn, Ca-Pb, Ca-U, Cd-Zn, Zn-Cu. Contrary, the bioavailability of the divalent cations Ca, Fe, Cu, and Zn can be enhanced by certain chelating substances, such as unidentified factors in meats or ascorbic acid, that promote their enteric absorption (WHO 2005). Ca is more readily absorbed in an acid milieu in the intestines (Wynn et al. 2009, Burckhardt 2008), and in general more readily absorbed from water than from food.

Scientific studies have shown that Ca, Mg, and HCO_3 when present in optimum concentrations in drinking water might play a significant role for a healthy body

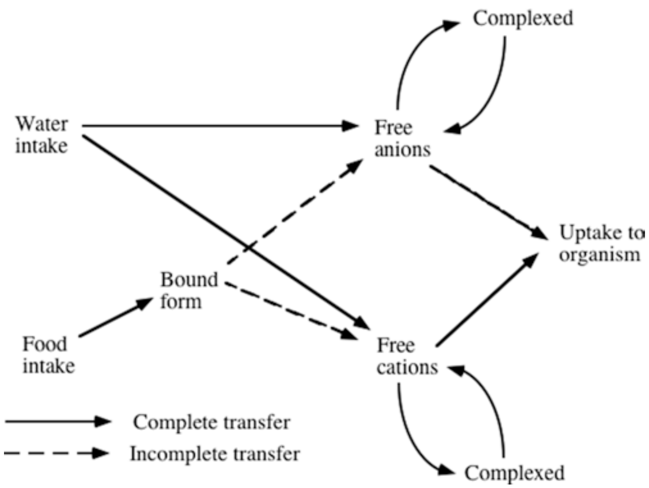

Fig. 2.2 Model for the gastrointestinal uptake of mineral elements in humans (I Rosborg)

(e.g. Schroeder 1966, Rylander 2008). As, F, Se, Pb, Cu, Fe, Mn, and Na are other elements that are readily absorbable from water (Yang et al. 1988, Mudur 2000, Singer et al. 1985, Parr 1996, Pettersson and Rasmussen 1999, Salonen et al. 1992, Mena 1981, Du et al. 2002). Concentrations of these micronutrients in drinking water are much lower than concentrations of Ca, Mg, HCO_3 and SO_4, but compared to the daily intake, certain waters give a substantial contribution, especially for persons with special needs, as infants or the elderly. A valuable indication of eventual need of minerals from drinking water is obtained from element concentrations reflected in body tissues as measured in one's hair (Rosborg et al. 2003). Also blood serum can be used for this purpose, as animals given Zn or Mg dosed in their drinking water got significantly higher concentrations of these elements in their blood serum, than animals given the same elements and in much higher doses in food (Kozisek 2005) (Fig. 2.2).

2.3 Minerals from Drinking Water – Contribution to the Daily Intake

I. Rosborg

Approximately 20 mineral elements are essential for humans. Drinking water may under certain conditions provide a substantial contribution to the RDI, Recommended Daily Intake (Rosborg 2005). The aim of Table 2.3 is to give an indication of the diversity of mineral content of different types of drinking water, depending on bedrock origin and treatment processes.

Table 2.3 Contribution of minerals from studied waters, assuming a daily intake of 2 L, as percentage of RDI, Recommended Daily Intake, or the older parameter Recommended Daily Allowance, for adults (70 kg) or estimated daily intake (Rosborg 2005)

	Water contribution to daily intake (percent)								
Source of water	Ca	Mg	P	Na	K	Cl	Fe	F	Mn
Well water	0.4–33	0.3–4.2	0–14.6	0.1–10	0–2.2	0.3–9	0–46	0–62	0.08–13
Municipal water	2.3–13.4	0.9–6.9	1.0–12	0.5–7.6	0.05–0.4	0.4–1.5	0–0.3	14–44	0–3.0
Bottled water	2.7–72	0.2–62	0–144	0.1–65	0.03–13.4	0.03–11	0–1.3	14–218	0–3.2

	Water contribution to daily intake (percent)								
Source	Cr	Se	Mo	V	Ni	B	Co	Li	Cu	Zn
Well water	0–2.4	0.2–19	0–18	1–42	0–127	0–3	0–406	n.a.	0–256	0–3
Municipal water	0.7–2.4	0–0.9	0–4	4.4–12	2–31	0.2–5.6	0.9–2.8	0.6–12	0–4.2	0–0,6
Bottled water	0–69	0–5	0–29	0–1360	0–50	0–24.3	0.3–17	0.1–119	0–1.2	0–1.5

The Reference Daily Intake or Recommended Daily Intake (RDI) is the daily intake level of a nutrient that is considered to be sufficient to meet the requirements of 97–98% of healthy individuals. The Recommended Dietary Allowance or RDA (sometimes referred to as Recommended Daily Allowance) is defined as “the average daily dietary intake level that is sufficient to meet the nutrient requirements of nearly all healthy individuals (approximately 98 percent)” (WHO 1996). Percentage is in general calculated on RDI/RDA according to Bowman and Russell (2006), but also Oberbeil (2000), NSFA (1997), Wilhelmsson (1997), Greer and Woodward (1987).

As can be seen from Table 2.3 the contribution of Ca from some well waters was as low as 0.4%, while others provided over 30%, and one label of bottled water from continental Europe provided 72% of the daily recommended intake for Ca. Contribution of Mg in the studied Swedish well waters or municipal waters varied from 0.3 to 6.9%, which indicates low Mg in the studied bedrock in general, while one label of bottled water could support a contribution of 69%. One label of Swedish carbonated bottled water was supplemented with Na salts, and contributed 65% of the normal daily intake, and it was therefore not recommended for people suffering from cardiovascular diseases (Rosborg et al. 2005). When this bottle was left open over night, and the carbonic acid was released as CO_2, the taste was extremely salty. On the other hand, the waters from central Europe that were very high in Ca and Mg, around 300 mg/L of Ca and 95 mg/L of Mg, and the bottled water that had very high HCO_3 concentration, over 1 g/L should be regarded medical waters, and used for people suffering from acidosis and subsequent diseases, e.g. cardiovascular diseases, osteoporosis, diabetes and even some forms of cancer. One acid well water gave 250% of Cu (from pipes), and one alkaline 46% of Fe (from bedrock). Both elements may cause intestinal disturbances, especially diarrhoea in sensitive humans, if the concentrations exceed approximately 1 mg/L (Banner and Tong 1986, Laine et al. 1988, Pettersson and Rasmussen 1999). Some specific waters also gave substantial contributions of Si, F, Co, and Li.

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Chapter 3
Macro-minerals at Optimum Concentrations – Protection Against Diseases

Ingegerd Rosborg and Frantisek Kozisek

Abstract There is a high content of minerals in so-called hard groundwater/drinking water, in areas with especially limestone, some kinds of sandstone and shales. Studies have shown lower incidence rates of different diseases in such areas. Calcium, magnesium and hydrogen carbonate from drinking water decrease the risk of especially cardiovascular diseases, osteoporosis, probably also cancer and diabetes. Hydrogen carbonate (HCO_3) counteracts metabolic acidosis, and decreases loss of Ca and Mg via the urine. Sulphate (SO_4) together with Mg may be active against constipation, but at too high level this water may cause diarrhoea. Ca and F (see further Chap. 4) in drinking water explains a great deal of the variation in the numbers of decayed, filled and missing tooth surfaces. However, there are some optimal ranges of the minerals to be only beneficial for health as high concentrations may be related to other health risks. Scientific studies also show that microelements like Se, Mo, Li and Cr from drinking water are important. Water softeners with NaCl, where Ca and Mg are more or less eliminated and exchanged for Na, can provide sodium (Na) levels of over 300 mg/L and cause especially elevated blood pressure. Water should not be softened to levels <8 °dH (<1.4 mmol/L). In the era of desalination, which produces drinking water with exceptionally low levels of mineral elements, even if the water is re-mineralized or pH-adjusted to avoid corrosion, such water may be harmful to sensitive individuals; e.g. those with low mineral intake from food. This will be expensive for society, mostly due to higher costs for healthcare, which recently has been estimated in a Danish study, but also, e.g., due to corrosion of pipes and installations. Suggested ranges for Ca, Mg, HCO_3 and SO_4 are: Ca 30–80 mg/L, Mg 10–50 mg/L, HCO_3

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100–300 mg/L and SO_4 25–100 mg/L, with Ca:Mg: 2–3:1. So far WHO (World Health Organisation) has not established minimum accepted concentrations for these elements.

3.1 Hard, Alkaline Water and Protective Effects at Optimum Concentrations

Water originating from soils rich in limestones, certain sandstones and greenstones (basic and basaltic rocks) is generally rich in minerals, and is labelled “hard water”. Water with high levels of minerals is formed as a result of a series of physical and chemical actions which occur over a long period of time (Fig. 3.1).

The hardness of water is a measure of the content of divalent metals, especially Ca^{2+} and Mg^{2+}. Waters from granite or some kinds of sandstone contain very small amounts of these minerals, and are referred to as being “soft”. Hardness is often expressed in °dH, “German degrees”, where 1°dH corresponds to 10 mg/L CaO, approximately 7.1 mg/L Ca (VAV 1994), but contemporary correct units are mmol/L (1 mmol/L = 5.6 °dH) or mg/L as $CaCO_3$. Several scales to represent hardness were developed. One of these scales is shown in Table 3.1.

Substantial concentrations of micro-elements, appearing at µg/L, such as Mo, Se, V and Cr are also generally present in hard water (Rosborg et al. 2002). An older American ecological epidemiological study stated that the death rates due to high blood pressure and arteriosclerosis were higher in cities where the drinking water

Fig. 3.1 Komstad limestone quarries (SGU 2014). Water from soils rich in limestones is rich in minerals

Table 3.1 Hardness in water as expressed in °dH (VAV 1994)

Hardness	°dH
Very soft	0–2
Soft	2–5
Mean hardness	5–10
Hard	10–20
Very hard	>20

had low conductivity, i.e. water having lower concentrations of Ca, Mg, Na, K, HCO_3, SO_4 and Ba, as well as of Cl, Si, Li, Sr and V, but often higher concentrations of Cu (Schroeder 1966).

Costi et al. (1999) concluded that a regular life-long daily intake of drinking water with highly bio-available Ca may be of importance for maintaining Ca balance and improving spinal bone mass. Ca-rich mineral water supplementation for 1 year showed an increase in bone mass density in postmenopausal women (Cepollaro et al. 1996).

Dozens of studies suggest that Ca and Mg in hard drinking water may affect the Ca and Mg status in bodies, and give clear indications that Ca and Mg are protective against premature death from cardiovascular diseases (e.g. Rubenowitz et al. 1999; Rylander et al. 1991; Monarcha et al. 2006) as well as from cerebrovascular diseases (Sakamoto et al. 1997; Yang 1998). A systemic review and meta-analysis of 14 most valid epidemiological studies investigating the association between cardiovascular disease and drinking water hardness brought convincing epidemiological evidence about the protective role of Mg in drinking water, as a pooled odds ratio showed a statistically significant inverse association between Mg and cardiovascular mortality (OR 0.75 (95%CI 0.68, 0.82), $p = 0.001$). It means that the highest exposure category (people consuming drinking water with magnesium 8.3–19.4 mg/l) was significantly associated with a decreased likelihood of cardiovascular mortality (by 25%), compared with the baseline, i.e. people drinking water with a Mg content of 2.5–8.2 mg/l (Catling et al. 2008). Two recent and independent meta-analyses confirmed these findings and also found significant protective effect of water calcium on cardiovascular diseases (Gianfredi et al. 2017; Jiang et al. 2016).

In a more recent systematic review with meta-analysis (Gianfredi et al. 2017), seven studies were retained from an initial list of 643 potentially eligible articles. Subjects exposed to the highest concentration versus those exposed to the lowest concentration were compared. The result suggests a protective effect of Ca and Mg on CVD prevention. However, the researchers conclude that the high heterogeneity and the existence of publication bias limits the robustness and generalizability of these findings. In addition, Rosenlund (2005) did not find this CVD prevention by hard water. Yang et al. (1999a, b) also found that drinking water hardness was significantly negatively correlated to the formation of different forms of cancer. One study showed that hard water could be protective against low birth weight (Yang et al. 2002), and another against cognitive impairment in the elderly (Jacqmin et al. 1994).

Better Human Health in Areas with Readily Weathered Sandstone, Shales or Claystones Than in Areas with Hard Weathered Andesites and Basalts

In a recent study from The Slovak Republic, where 90% of the population drink groundwater, Rapant et al. (2014) compared the health of inhabitants in different geological environments, by comparing number of deaths per 100.000 inhabitants. They found that Neogene Volcanics (andesites and basalts) had the least favourable impact on the health of the Slovak population, while Paleogene Flysch geological environment (sandstones, shales, claystones) had the most favourable impact, especially on cerebral infarction and stroke. Thus, there were more than 70% higher number of deaths per 100,000 inhabitants due to cerebral infarction and stroke in Neogene Volcanic regions than in Paleogene Flysch geological environment, the digestive system (55%), circulatory system, endocrine and metabolic system (almost 40%), and malignant neoplasms (tumours, more than 30%). The results can likely be associated with deficit contents of Ca and partly Mg in groundwater from the Neogenic Volcanics (Ca average 43.15 mg/L and Mg 14.7 mg/L), which for Ca is only half the level compared to Palogene sediments (Ca average 88.53 mg/L and Mg 19.67 mg/L. HCO_3 (average 138.29 mg/l and 287.65 mg/L, respectively) may also have an impact on the difference in health between these two areas (editor's comment), since its buffering properties are important to avoid acidosis, causing Ca and Mg loss via urine.

Thus, these Slovak authors question the WHO Universal Declaration, stating that lifestyle (the way of life and work) accounts for 50% of population health, since there were no significant differences regarding these aspects found between these two areas. The WHO stated that environmental factors only account for about 10–20% of population health. The findings from the Slovak study are in accordance with the results from the study of well waters, hair and health of women, where women living in an area dominated by primary rock bedrock reported more negative health changes during the time they had been drinking their specific well water than women in an area dominated by limestone bedrock (Rosborg et al. 2002, 2003; Rosborg 2005; Rosborg and Nihlgård 2018). Rapant et al. (2015) suggested that the recommended levels of Ca and Mg in Slovakia should be increased from current Ca: more than 30 mg/L and Mg: 10–30 mg/L to Ca: more than 89 mg/L, and Mg: 24–96 mg/L. The presented optimum range for Mg was 42–78 mg/L. Their study was based on ReI (relative mortality for cardiovascular diseases) data in relation to chemical composition of groundwater in the Slovak Republic.

A Russian study focused on morbidity and physical development of 7658 adults, 562 children and 1582 pregnant women and their newborns in two areas supplied with different waters (Lutai 1992). One of these areas was supplied with water having low mineral concentrations, mean values: TDS 134 mg/L, Ca 18.7 mg/L, Mg 4.9 mg/L, HCO_3 86.4 mg/L. The other area was supplied with water having relatively high mineral concentrations, mean values: TDS 385 mg/L, Ca 29.5 mg/L, Mg 8.3 mg/L, HCO_3 243.7 mg/L. Concentrations of SO_4, Cl, Na, K, Cu, Zn, Mn and Mo were also determined. The populations of the two areas did not differ from each other in eating habits, air quality, social conditions or duration of residence in the respective areas. People from the area with lower TDS showed higher incidence rates of goiter, hypertension, ischemic heart disease, gastric and duodenal ulcers, chronic gastritis, cholecystitis (eliminated gallbladder) and nephritis (inflamed kidneys). Children living in that area also exhibited slower physical development and more growth abnormalities, pregnant women suffered more frequently from oedema and anaemia, and newborns showed higher morbidity. The lowest morbidity was associated with water having concentration of Ca 30–90 mg/l, Mg 17–35 mg/l, HCO_3 250–500 mg/L and TDS 400 mg/l (for hydrogen carbonates contained in water) (Lutai 1992). The authors concluded that such water could be considered as the most suitable from a physiological point of view. Data from a survey of articles suggested that a mixture of Ca and Mg, along with HCO_3, is the appropriate measure to avoid deaths from CVD, cardiovascular diseases, but the exact proportion of the different minerals to be used is not known (Rylander 2014).

These research studies support the general knowledge that both too much and too little mineral salts (TDS) may be equally harmful. Thus, cognitive function increases with calcium level up to a certain point and then might decrease as calcium continued to increase above about 90 mg/L (Emsley et al. 2000). In addition, studies during 1970–1990 in Russia suggest that regular and long-term intake of extremely mineral-rich water (TDS more than 1000–2000 mg/L) is a risk factor for developing various diseases of the excretory system (kidneys and urinary tract) and gastrointestinal tract, affecting female reproductive functions, development problems in children, arthritis and higher rate of calculi (urolithiasis and cholelithiasis) (Shtannikov and Obyedkova 1984; Shtannikov et al. 1986; Lagutina et al. 1990; Muzalevskaya et al. 1993; Rylova 2005). Animal experiments with rats consuming drinking water with high TDS (above 2000 mg/L) showed acceleration of processes of ageing as well as certain embryotoxic effects (Gabovich and Uzhva 1975a, b; Shtannikov et al. 1985). Petrov and Grebenkin (1964) made experiments with both laboratory animals and human volunteers. Long-term consumption of water with high levels of HCO_3 decreased excretion of uric acid and increased its deposition in tissues. These studies all give a clear indication that too little and too much may both present health risks, implying the need for recommended ranges of minerals in drinking water.

Basically, WHO (2005) only relates to the nutritional value of Mg and F from drinking water and their protection against cardiovascular diseases and dental caries, respectively. Several other mineral elements and ions in drinking water are also discussed, but not properly reflected in the context of the book: water as a source of beneficial essential minerals.

Substantial Ca and F Levels in Drinking Water Is Protective Against Caries, Especially for Families with Low Income: Costs Related to Non-reminerlized and Remineralized Desalinated Water, RO Water

Substantial concentrations of drinking water minerals are especially important for people at risk of low intake of minerals from food, e.g. families with low income. Thus, in a recent Danish study Ca and F in drinking water together explained 45% of the variation in the numbers of decayed, filled and missing tooth surfaces (DMF-S) in a mathematical model among 52,057 15-year-old schoolchildren. Recommended levels were 0.75 mg/L of F and 90 mg/L of Ca (Bruvo et al. 2008). Another mathematical model indicated that a decrease in family income by 100,000 Danish Kronor needed an increase in Ca drinking water concentration by 37 mg/L and 0.24 mg/L of F to maintain unchanged caries experiences. In addition, from a case study it was calculated that a reduction of Ca from 120 mg/L to 33 mg/L by softening, may increase the average caries experience by 46%, clearly indicating the negative effects on teeth by softening of water (Arvin et al. 2018). The authors conclude that if F is added to drinking water, CaF_2 should be used, to include Ca in the supplementation. Another expanded model showed negative correlation between concentrations of Ca, F, pH and HCO_3 and DMF-S, whereas it was positive for chloride (Bruvo et al. 2008).

Other researchers also pointed out Ca from drinking water as important for tooth health, e.g. Glass et al. (1973) and Mills (1937).

In another Danish study **economic consequences of consumption of desalinated water** (generally RO (Reverse Osmosis-treated seawater) was evaluated. Cardiovascular diseases, dental caries, atopic eczema, lifetime of dish and clothes washing machines, heat exchangers, bottled water consumption and soap usage were investigated. Effects were calculated for a scenario where 50% of Copenhagen's water supply is substituted by desalinated water. The water presently used is hard ground water, with Ca 117 mg/L, Mg 18.6 mg/L, HCO_3 348 mg/L, and F 0.48 mg/L. Health impacts had the highest contribution to the impact on the price per m^3, when all these factors were taken into account. Thus it was stated that without re-mineralization the total impact on water price was negative; €-0.44/m^3, but with re-mineralization (proposed optimum: Mg >10 mg/L, Ca 40–50 mg/L, F 0.5–1 mg/L) it would even be positive (€0.14/m^3). Expected costs of physical changes in Copenhagen with 50% conventional sources replaced with desalinated seawater for dental health is €6.2/case/year, cardiovascular diseases €3731/case/year. This can be compared to the costs for fluoridation, which is estimated at €0.35/person/year, and Mg/Ca addition €0.70/person/year (Rygaard et al. 2009).

Fig. 3.2 Rubble-stones, granite (SGU 2014). Water from gneiss and granite bedrock is poor in minerals

During the 1960s and 1970s the southernmost parts of Scandinavia suffered from acid rainfall, caused by extensive combustion of coal (SO_2 emission with subsequent formation of sulphuric acid). The "Acid Rain" led to serious damages to aquatic life and vegetation (Bertills and Hanneberg 1995; Nihlgård 1997). One Swedish study on the influence of this man-made acidification on humans was performed, the only one in the world so far (Rosborg et al. 2002, 2003; Rosborg and Nihlgård 2018) (Fig. 3.2).

Subjects were chosen among female non-smokers who had been drinking their specific well water for at least 5 years. Wells without filters were chosen. Around 40 elements in well water and hair were analysed. The results showed that the concentrations of essential mineral elements, such as Ca, Cr, Se, K, HCO_3, SO_4 and Mo were significantly lower in acid well waters than in alkaline. Table 3.2 clearly demonstrates the differences in concentrations with respect to Ca, Mg, HCO_3, SO4 in acid well waters compared to alkaline well waters. pH levels were all initially <pH 6 in acid well waters. Through transportation and storage in a freezer they increased by approximately 0.5 pH units.

As can be noted from the table, the median concentrations of Ca in alkaline well waters were 6 times higher than in acidic wells. Mg is present to very low concentrations even in the alkaline soils in the alkaline area, which is also shown in the well waters. HCO_3 was almost 14 times higher in alkaline well waters than in acid ones, see Fig. 3.3.

Table 3.2 Median concentrations and ranges of some studied minerals in acid (granite bedrock) and alkaline (limestone bedrock) well waters in Sweden (Rosborg et al. 2002)

	Median and range acid wells	Median and range alkaline wells	Unit
pH	6.0 (4.45–6.45)	7.6 (7.1–8.9)	
Conductivity	108 (49–241)	297 (53–890)	µS/cm
Ca	9.8 (1.6–25.2)	61 (26–131)	mg/L
Mg	1.7 (0.5–5.7)	2.1 (0.5–6.6)	mg/L
HCO3	11.4 (0–51)	141 (68–300)	mg/L
SO4	10.8 (5.1–27.3)	26.1 (2.7–180)	mg/L
K	2.5 (0.2–30)	3.6 (0–45)	mg/L
Na	6.2 (1.9–21)	6.4 (2.6–101)	mg/L
Cl	11.9 (3.9–68.4)	18.1 (4.5–180)	mg/L
Mo	0.1 (0.01–0.26)	3.5 (0.29–14.8)	µg/L

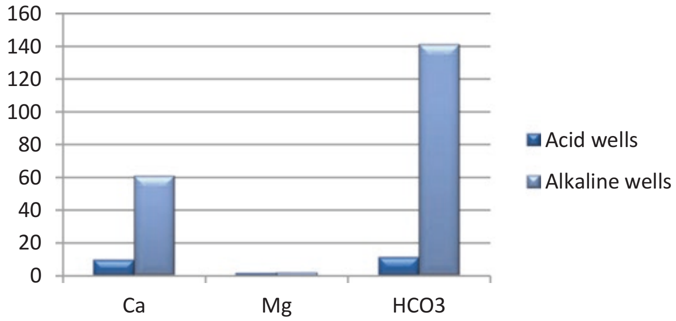

Fig. 3.3 Median concentrations of Ca, Mg and HCO_3 in acidic vs alkaline well waters (Rosborg et al. 2002)

Cu concentration was well over 3 mg/L in one acid well water, due to dissolution from pipes, indicating the risk of problems with diarrhoea and subsequent symptoms, especially for infants drinking formula prepared from the well water.

Well water minerals were reflected in hair, especially Ca, Sr, Pb and Mo; see Table 3.3. Hair nutrient analysis was chosen to mirror body minerals, as the first three cm of hair cut close to the scalp reflect the history of nutrient intake during the last 3 months (Rosborg et al. 2003).

Like in the waters, hair of women from the alkaline area was median six times higher in Ca than hair of women from the acid area, clearly indicating the importance of Ca from drinking water, Fig. 3.4.

Mo is needed for Fe mobilization and detoxification in the liver (Bowman and Russell 2006). Mo in well water was mirrored in hair of women (Rosborg et al. 2003). Median levels of Mo in hair are presented in Fig. 3.5.

The interviews with women clearly indicated that soft acid and mineral poor water was linked to a higher number of health changes during the time the women had been drinking their well water, at least 5 years (Rosborg 2005) as shown in Fig. 3.6.

Table 3.3 Median and range concentrations of some elements in hair of women drinking acid and alkaline well waters, respectively, for at least 5 years (Rosborg et al. 2003)

	Median acid	Range	Median alkaline	Range
Ca µg/g	283	50–2830	1290	231–5630
Copper µg/g	47.4	6.1–716	19.8	8.3–179
Mg µg/g	26.4	9.5–424	32.2	7.2–299
Sulphur µg/g	42500	30200–50200	43800	41480–51700
Molybdenum ng/g	9.0	9.0–190	29	9.0–311
Strontium ng/g	624	46–8610	2640	312–13200
Lead ng/g	755	68–9480	612	109–2180

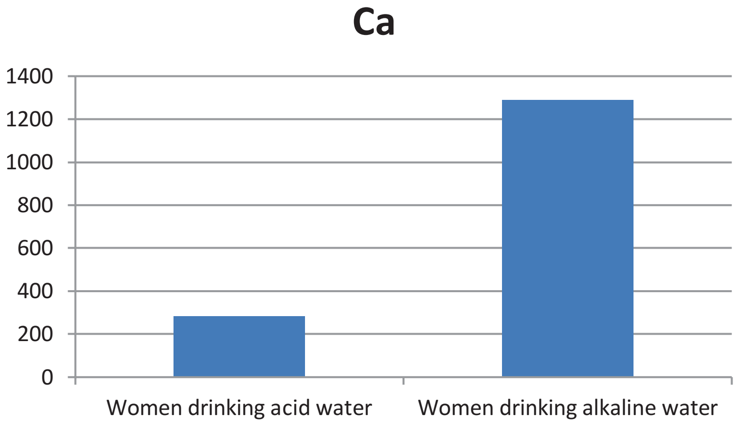

Fig. 3.4 Median calcium levels in hair (µg/g) of women drinking acid and alkaline well waters, respectively (Rosborg et al. 2003)

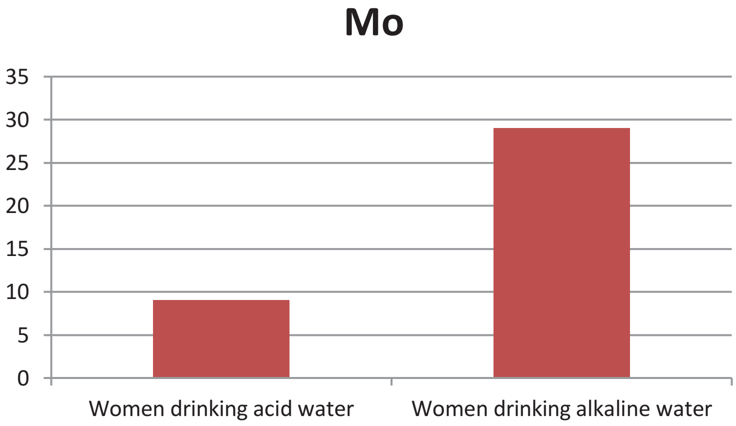

Fig. 3.5 Median molybdenum (Mo) levels (ng/g) in hair of women drinking acid and alkaline well waters, respectively (Rosborg et al. 2003)

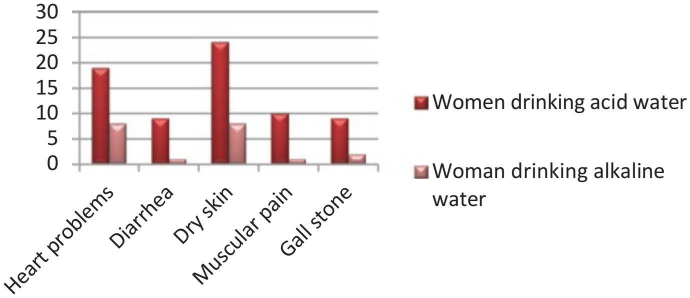

Fig. 3.6 Reported health changes during the time women had been drinking their specific well water, at least 5 years (Rosborg 2005)

These findings are in accordance with the results from studies on the differences in mineral content and health of people drinking hard water versus soft water, as reported above (e.g. Schroeder 1966; Lutai 1992) (recall that acidic waters are soft and alkaline waters are generally hard). Apart from the trend to decrease sulphur oxide emissions in Central Europe, the addition of limestone to streams and lakes, and in some cases in forests, has minimized the damage to the flora and fauna in 80–90% of cases. Additionally, Al in some drinking waters has decreased substantially (EPA Sweden 1991). However, the need for treatment of people suffering from acid well waters has not been addressed.

WHO (2005) does not reach the conclusion that regulations on minimum hardness, or Ca, Mg and HCO_3, is practical, based on today's knowledge. Instead WHO states that confounding factors, e.g. softening filters, daily water intake, socioeconomic differences, climate, rainfall or other exposures which may impact especially cardiac functions, and those that can be associated with Ca and Mg intake from drinking are not properly specified in some studies. WHO also stated that toxic metals may be present in soft waters, due to the results of corrosion, such as Cu and Pb, or metals released from soils and bedrock, such as Al and Cd, making soft water potentially toxic. However, the number of studies clearly show the importance of drinking water as a source of essential minerals is numerous. Thus, we find it impossible to disregard the importance of the mineral composition of drinking water.

This view is also supported by the statement of two prominent epidemiologists R. Calderon and P. Hunter. "Information from toxicological, dietary and epidemiological studies supports the hypothesis that a low intake of magnesium may increase the risk of dying from, and possibly developing, cardiovascular disease or stroke. Thus, not removing magnesium from drinking water, or in certain situations increasing the magnesium intake from water, may be beneficial, especially for populations with insufficient dietary intake of the mineral. This raises a significant policy issue. How strong does the epidemiological and other evidence need to be before society acts to reduce a potential public health threat rather than await further evidence that such a threat is real? Such a decision is a political rather than a purely public health issue. There is a growing consensus among epidemiologists that the epidemiological evidence, along with clinical and nutritional evidence, is already strong enough to suggest that new guidance should be issued" (WHO 2009).

In the recent study by Rapant et al. (2014), ten chemical elements/parameters in groundwater were defined as the most significant for cardiovascular diseases in the Slovak Republic: Ca + Mg (mmol/L), Ca, Mg, TDS, Cl, HCO_3, SO_4, NO_3, SiO_2 and PO_4. The obtained results document the highest relationship between cardiovascular diseases and groundwater contents of Ca + Mg (mmol/L), Ca and Mg. The following limit values were set for the most significant groundwater chemicals/parameters: Ca >50 mg/L, Mg >25 mg/L and Ca + Mg >2 mmol/L. These limit values are about twice as high in comparison with the current Slovak guideline values for drinking water (Rapant et al. 2014, 2017). The authors conclude: "Based on the achieved results, we recommend that the World Health Organization consider revising their definition of drinking water quality standards for Ca and Mg contents and water hardness."

Often one toxic element is reduced or eliminated from drinking water, since there is a guideline value set by WHO, EU or national authorities. However, the chosen technology may also reduce the levels of essential elements, e.g. Ca, Mg and/or HCO_3. One example from the Czech Republic is described in the box.

Balancing Two Different Chemical Risks

Current regulatory schemes for drinking water safety cover a list of the most common chemical pollutants, mostly based on historical experience (nitrates, lead, arsenic etc.), but partially also on knowledge on emerging contaminants. A number of these chemical substances – at concentrations found in drinking water – have only hypothetical or negligible health risks, nevertheless, due to regulation, water producers are forced to manage every, even a small non-compliance with established limits. Management options include installation of new water treatment technology, selection of new source of water or mixing water from polluted and unpolluted sources. As most of these regulatory schemes ignore parameters which have much higher health risk and population impact if present in water in too low a level (magnesium, bicarbonates, calcium), accepted remedial options may in fact represent much higher population risk if these aspects are not taken into account. Typical example is removing some element by reverse osmosis, which at the same time substantially reduces the levels of essential and health-supporting minerals in drinking water. Another example of balancing two different chemical risks may be illustrated with results from the study done by the Czech National Institute of Public Health (NIPH) for one Czech municipality.

The Czech town X. of 10,000 population uses local groundwater sources polluted by both tertachloroethene (PCE) and trichloroethene (TCE). Water is treated by aeration (stripping) and concentration of sum TCE+PCE in treated water is about the limit value of 10 μg/l. The health risk from this level of pollution in this town is about 1 case of cancer per 25 years. The operator consid-

(continued)

ered two options for improvement: either to renew and intensify treatment of local water or to connect with adjacent water supply with unpolluted groundwater. However, local groundwater has magnesium level about 30 mg/l, but adjacent water supply only 5–8 mg/l. For this reason, the operator turned to the NIPH to calculate health risks from both options to have a scientific ground for proper decision-making.

If the town switches to adjacent source with much lower Mg content for consumers, it would represent about 20–30% higher risk of death from cardiovascular diseases (Catling et al. 2008). If we take into account high incidence of cardiovascular diseases in European population, the change of water source may lead to several deaths per year – in comparison with the "benefit" of 1 case of cancer per 25 years. The operator decided not to switch the source, but continue to treat local water to avoid substantial increase in health risk for consumers (Kozisek 2018, unpublished).

3.2 Some Macro-minerals in Hard, Alkaline Water

3.2.1 Introduction to Macro-elements

The concentrations of Ca, Mg, HCO_3 and SO_4 in hard drinking water are generally 100–1000 times higher than micro-elements. The effects of these macro-elements from drinking water on humans have been scientifically studied since the 1950s and a considerable amount of information is currently available. Na is generally not needed from drinking water but may in some sources be present naturally in higher concentrations, but is always elevated when softening filters are used. K concentration in drinking water is generally very low. See further Table 3.5.

3.2.2 Calcium (Ca)

Function in the body Ca is the most abundant element in the body and supports strength, weight and hardness in teeth and bones, with well over 90% in bone tissue. Ca also acts as a regulator of the activities of parathyroid hormone, calcitonin and vitamin D. Ca decreases blood pressure and is required for vascular and other muscular contraction. Cell membranes, nerve impulses, breast milk, pH regulation, and the release of hormones are also dependent on adequate Ca levels. The Ca concentration in cells is strictly regulated in healthy individuals, and excess levels in blood plasma lead to excretion of Ca through the kidneys or bonding to proteins. The daily recommended intake of Ca is approximately 200 mg for infants, 1300 mg for teenagers and 1000 mg for adults (FNB 2012; NIH 2013). Absorption of Ca takes place in the whole gastrointestinal (GI) tract, and its bioavailability depends on the concentration of ionized Ca in the small intestine. Phytate, phosphorus and triglycerides in the intestines bind to Ca, decreasing its uptake (Porkka et al. 1991). When plasma-Ca decreases, parathyroid hormone PTH is activated and Ca is released from bone tissue, leading to osteoporosis (FNB 2012; Bowman and Russell 2006).

Deficiency In Danish men, a tenfold increase in dairy calcium intake was significantly associated with a decreased risk of tooth loss (Adegboye et al. 2012). Lack of Ca may also lead to rickets (Bowman and Russell 2006). Reeves and Chaney (2001, 2002) found that a low Ca intake by rats caused increased absorption and retention of Cd. Ca can also modify the utilization of other dietary elements. Romasz et al. (1977) fed rats with a wide range of dietary Ca. He found that if dietary Ca was increased, the concentrations of Cu in the liver increased, and Zn decreased. In addition, Ca, U, and Pb share transporters in the blood, and can be mutually inhibitory (WHO 2005).

Excess Kidney stones can be formed with excess Ca intake (Mirzazadeh et al. 2012). Other reported symptoms are constipation, excessive abdominal cramping, bloating, gastrointestinal symptoms, severe diarrhoea and abdominal pain (Lewis et al. 2012).

From drinking water A life-long regular daily Ca intake from drinking of highly bio-available Ca may be of importance for maintaining Ca balance and for improving spinal bone mass (Costi et al. 1999). An association between low Ca content of drinking water and fractures in children has been observed (Verd et al. 1992). As stated above, hard water can be protective against premature death from cardiovascular disease (CVD) and cerebrovascular diseases (e.g. Rubenowitz et al. 1999; Rylander et al. 1991; Sakamoto et al. 1997; Yang 1998), but some recent meta-analysis of the most advanced epidemiological studies confirmed this health effect for Mg but not for Ca (Catling et al. 2008). However, Stevanovic et al. (2017) found that two factors had a significant impact on the differences in morbidity from ischemic heart disease. These were Ca and Mg from food and drinking water. Even though the average daily water intake of respondents was less than 2 L, a significant difference in the higher intake of Ca and Mg from drinking water compared to the intake via food was found. Hard water is also protective against different kinds of cancer (Yang et al. 1999a, b), and cognitive impairment in elderly (Emsley et al. 2000). Apparently, the effect evens itself out at extremely high concentrations of Ca. Softening of water with addition of NaCl to decrease scale deposition of Ca salts increases the Na content, as Ca is substituted with Na in the water. Such water has been shown to increase blood pressure (Xie et al. 2001; Kousa et al. 2006; Njelekela et al. 2001).

Mg and Ca may act as metabolic antagonists. One Finnish population-based ecological study showed that a high Ca:Mg ratio in drinking water and thus deficiency of Mg in the diet and in water significantly increases the risk of acute myocardial infarction (AMI). A one unit increment in the Ca:Mg ratio increased the risk by 3.1%, and a 1 mg/L increment in Mg concentration decreased the AMI risk by 4.9% (Kousa et al. 2006).

On the other hand, hard water may be related to eczema, due to more dermal exposure from cleaning the body with water than due to ingestion (Chaumont et al. 2012). Kidney-stone-forming patients showed an increase in urinary Ca/Mg creatinine excretion as drinking water hardness was increased (Mirzazadeh et al. 2012).

Durlach et al. (1989) recommends a Ca:Mg total intake ratio of 2:1. Rapant et al. (2015) suggest >89 mg/L for Ca in drinking water. No health-based guideline value has been proposed or regulatory established on the WHO or the EU levels (WHO 2017, EU 1998).

Suggested range Risk-reducing Ca concentration appears to be 30–80 mg/L, Ca:Mg 2–3:1. Together with high Mg, SO_4 and other ions TDS should not exceed 1 g/L as an absolute upper limit, but <500 mg/L is recommended. A suggested lower limit of TDS is 100 mg/L.

3.2.3 Magnesium (Mg)

Function in the body Mg acts as a cofactor for nearly 300 enzymes important for energy production and storage, carbohydrate metabolism, heart, muscles, bones and nerve impulses (Bowman and Russell 2006). In particular, an adequate Mg level in the heart muscle is crucial for normal maintenance of the heart beat rhythm, and the coronary arteries that supply heart muscles with oxygen-rich blood (Altura and Altura 1987). Current RDI for Mg is about 280–350 mg for different populations (NSFA 2012). Recently some experts have suggested a higher RDI value of 450–500 mg for prevention of coronary heart disease (Altura and Altura 2009). Diabetic people may require higher Mg intake due to higher urinary loss. Obese people also need more Mg. There are numerous studies on the importance of sufficient Mg intake. In a study of 577 pairs of brothers it was found that the brothers living in Ireland had Mg intake of more than 400 mg/day. These brothers had approximately 40% lower CVD deaths, when compared to the brothers living in Boston, with dietary Mg intake of 274 mg/day (Brown et al. 1970). Cells of the heart muscles rich in Mg can survive for a longer time when subjected to oxygen-deficient environment (Faghihi et al. 2008). In one study, supplementation with Mg during pregnancy decreased the risk of gestational hypertension (Rylander and Bullarbo 2015).

Deficiency Magnesium deficiency may be caused by excessive alcohol intake, certain medications, such as diuretics, reduced absorption, due to intestinal disturbances, or insufficient nutritional intake due to high consumption of refined food. Loss of appetite, muscle spasm, fatigue, weakness, neuromuscular excitability, osteoporosis, diabetes mellitus, and cardiac complications, such as, hypertension, dys-rhythmia, angina pectoris, and acute myocardial infarction may be signs of Mg deficiency (Bowman and Russell 2006). Some women fed on a diet poor in Mg developed abnormal heart rhythm and increased glucose levels in their blood serum. When they switched over to a diet containing higher Mg these abnormalities disappeared (Nielsen et al. 2007). Mg-deficient coronaries undergo reduction in the diameter of the coronaries. This can reduce blood flow and cause sudden death (Turlapaty and Altura 1980). Magnesium homeostasis can be disturbed by an insufficient intake or an increased urinary excretion of Mg urinary excretion is induced by an increased acid load, following excessive exercise or the consumption of large amounts of proteins (Remer 2001; Rylander et al. 2006, 2009), which will increase the acidity of the urine, and decrease the re-absorption of Mg (Remer 1995). Too much sugar, bread and alcohol also cause urinary loss of Mg (Wilhelmsson 1997).

Excess Symptoms of excess Mg can be similar to Mg deficiency, and may include changes in mental status, diarrhoea, loss of appetite, muscle weakness, difficulty breathing, extremely low blood pressure, and irregular heartbeat. However, it seldom happens in persons with normal kidney function, and is mostly due to excess Mg from supplements. Elevated Mg levels in the blood are generally treated with Ca, in order to balance Mg (Bowman and Russell 2006).

From drinking water 25 cities in the USA having the highest CVD mortality had water supplies that averaged 5.1 mg/L Mg and 75 mg/L HCO_3, while 25 cities with the lowest CVD mortality averaged 16.5 mg/L Mg and 127 mg/L HCO_3 in their drinking water. The cities receiving Mg-rich water also showed lower premature mortality from all causes of death (Schroeder 1966). The soils and groundwater of western Finland have approximately three times higher Mg content as compared to the soils and groundwater in the eastern parts of Finland. CVD mortality in the eastern part is approximately twice that in the western regions (Punsar and Karvonen 1979). In Sweden, the risk of dying of cardiac infarction was 34% lower if the drinking water had a concentration of Ca that exceeded 70 mg/L and Mg 9.9 mg/L (Rubenowitz et al. 1999). Towns receiving waters with a Mg concentrations of 20 mg/L had 35% lower mortality due to CVD, as compared to the towns where water supply had approximately 2 mg/L (Rubenowitz et al. 1996).

The most comprehensive review of epidemiological studies suggesting inverse relationship between water Mg (higher hardness) and CVD mortality was commissioned by the Drinking Water Inspectorate of England and Wales and prepared by University of East Anglia in 2005 (Catling et al. 2008). Two thousand and ninety-six papers were identified. A total of 115 underwent full article appraisal by two independent reviewers. Of the 12 highest quality studies, 9 presented evidence for a significant inverse association between water hardness and premature cardiovascular mortality. Five cross-sectional studies showed an inverse association between elevated levels of drinking water Ca and/or Mg and blood pressure and serum lipids which were observed in some, but not all, studies. One cohort study was conducted in Great Britain and found no association between drinking water hardness and cardiovascular disease. However, this study also suffered from poor exposure characterization. Meta-analysis of 14 analytical observational studies brought convincing epidemiological evidence to demonstrate the protective role of elevated Mg in drinking water. These results demonstrate that Mg concentrations 8.3–19.4 mg/L was significantly associated with a decreased likelihood of premature cardiovascular mortality (by 25%), compared with the baseline (Mg range 2.5–8.2 mg/L) (Catling et al. 2008).

A set of Taiwan studies, so far confirmed by epidemiological studies only from one country (Slovakia), suggest that Mg concentration in drinking water exceeding 10 mg/L is protective against some forms of cancer (Yang et al. 1999a,b). The Taiwan studies also reported that the risk of rectal cancer from THMs (trihalomethanes) was increased when the Mg level was low in drinking water (Kuo et al. 2010). There appeared to be a significant protective effect of Mg intake from drinking water and the risk of dying from colon cancer mortality (Yang and Hung 1998), prostate cancer development (Yang et al. 2000a) and death from breast cancer (Yang et al. 2000b). If the Mg concentration was higher than approximately 17 mg/L there were also fewer deaths due to diabetes (Yang et al. 1999c).

According to the WHO monograph *Nutrients in Drinking Water* (WHO 2005), one possible mechanism is that the Mg present in some hard waters is sufficient to prevent borderline Mg deficiencies in some persons, thereby reducing their liability to sudden cardiac death, as a result of arrhythmia following MIA (myocardial infarction).

It should be noted that the increased intake of Mg salts, especially $MgSO_4$, may cause diarrhoea (WHO 2017) (Epsom salts is a cure for constipation). Rapant et al. (2015) suggest 24–96 mg/L, optimum range: 42–78 mg/L, for Mg in drinking water. No health-based guideline value has been proposed or regulatory established on the WHO or EU levels (WHO 2017; EU 1998).

Suggested range The risk-reducing Mg concentration range appears to be 10–50 mg/L. The recommended upper limit is 150 mg/L. A Ca:Mg ratio of 2–3:1 is recommended.

Considering the laxative effect of both Mg and SO_4, a tentative upper limit is recommended to be (Mg + SO4) ≈ 400 mg/L. Together with high Ca, SO_4 and other ions TDS should not exceed 1 g/L as an upper limit, but <500 mg/L is recommended, and a suggested lower limit for TDS is 100 mg/L.

3.2.4 Hydrogen Carbonate (HCO_3)

Function in the body, deficiency/excess Hydrogen carbonate, HCO_3, is included in one of the pH-regulating systems of the body, the carbonic acid/hydrogen carbonate system. The pH of the body lies in a narrow range for proper function (Sonesson and Sonesson 2001). Blood should have a pH of 7.34–7.45. Carbon dioxide (CO_2) is formed in the carbohydrate metabolism and reacts with alkalinity in water (OH) to form hydrogen carbonate (HCO_3):

$$CO_2 + OH^- \leftrightarrow HCO_3^-$$

The HCO_3^- ions are absorbed in the body fluids and contribute to preserve the pH level (Sonesson and Sonesson 2001). Hydrogen carbonate in water in soils and bedrocks is formed by action of dissolved CO_2 gas on Ca and Mg carbonate present in soils or underground rocks. Drinking water as a source of HCO_3 for humans may be of great health importance.

The diet of the majority of people produces excess acids in the body, especially sugar, bread, cookies, sweets and wine end up as acids through digestion. A lower pH environment in the body may cause metabolic disturbances. Only a diet very rich in vegetables and fruits does not produce excess acids in body cells (Bowman and Russell 2006). Excess acids are extracted through the kidneys in healthy individuals. Age-related decline in kidney function may fail to remove the acids generated in the body, and the excess acids react with the alkaline reserve in bones and blood. The alkalinity needed to maintain the blood pH is supplied by the gradual loss of bone Ca and is therefore undesirable (Sellmeyer et al. 2001). This phenomenon is known as the beginning of metabolic acidosis.

As bones loose substantial alkalinity reserves and Ca, the blood pH may drop below 7.35, which is even more undesirable. This phenomenon is called chronic metabolic acidosis. Under these conditions in addition to the bones losing Ca, the muscle proteins also start to degenerate (Sonesson and Sonesson 2001). In addition, the oxygen-carrying capacity of blood is compromised at low blood pH and consequently affects the heart (Sellmeyer et al. 2001; Hu et al. 1993; Rylander et al. 2006). Increased loss of cardio-protective Mg due to increased urine acidity has also been found. Treatment of severe acidosis by Na and K hydrogen carbonate has improved patient health (Gannon et al. 2008; Makino et al. 2005; Wiederkehr and Krapf 2001), and reduced the bone resorption rate, decreasing osteoporosis (Wynn et al. 2010; Burckhardt 2008). A number of studies have shown that the extracellular pH (pHe) in cancers is typically lower than that in normal tissue and that an acidic pHe promotes invasive tumour growth in primary and metastatic cancers. Increased serum concentrations of sodium hydrogen carbonate ($NaHCO_3$) can be achieved by ingesting big amounts. Furthermore, consequent reduction of tumour acid concentrations significantly reduced tumour growth and invasion without altering the pH of blood or normal tissues (Silva et al. 2009). In another study, authors conclude that oral $NaHCO_3$ selectively increased the pH of tumours and reduced the formation of spontaneous metastases in mouse models of metastatic breast cancer (Robey et al. 2009).

However, Ca and Mg-salts (carbonates and hydrogen carbonate) are underestimated, but would bring Ca also to the body, which is important especially to those suffering from Ca deficiency.

From drinking water Generally, drinking water contains 20–400 mg/L HCO_3 (Aastrup et al. 1995). In non-carbonated water, the concentration of HCO_3 is dependent on the pH. At pH levels below 5, all HCO_3 combines with H^+ to form H_2CO_3, carbonic acid, and CO_2 is emitted. At pH above 8, most of the HCO_3 is in the form of CO_3^{2-}. Thus, the HCO_3 concentration is generally highest at pH 7–8 (Rosborg et al. 2002). From the days of health visits at spas, HCO_3 was known to neutralize acids, thereby decreasing acidosis, and to relieve symptoms in subjects with indigestion, constipation, irritable colon syndrome and gastric ulcers (Bergmark 1959; Hult 2007; Jones and Walter 2007; Petraccia et al. 2006). During the reaction of $HCO_{3,}$ with acids in the stomach, CO_2 is emitted, which may increase the volume of the stomach, and this effect may be pain relieving.

The earliest scientific report of very low HCO_3 in drinking water was made by a Japanese chemist who hypothesized that abnormally high premature mortality in Japanese youth, due to stroke (sudden death) could be a result of very low or negligible HCO_3 alkalinity in drinking water available from Japanese water sources (Kobayashi 1957). Elevated HCO_3 concentration in drinking water helps in minimizing urinary loss of Ca and Mg (Hu et al. 1993; Rylander et al. 2006).

After consumption of hydrogen carbonated water, significant reductions in total cholesterol were observed (Pérez-Granados et al. 2010). Hydrogen carbonated mineral water could be applied in dietary interventions to reduce cardiovascular risk and preventing osteoporosis (Wynn et al. 2009). However, it is necessary to keep in mind the coincident increased level of Na in such waters and the potential impacts on people with Na-restricted diet. In that case, $CaCO_3$, $MgCO_3$ or $KHCO_3$ is preferably used.

Data from intervention studies (Rylander 2008) using Mg, Ca and HCO_3 were reviewed. It was suggested that some negative health effects related to drinking water found in some studies may be caused by an increased urinary excretion of minerals induced by acid conditions in the body and that drinking water should contain sufficient amounts of HCO_3 to prevent this effect.

A panel of experts found that large geographical areas of the USA with the highest and lowest longevity have the following drinking water minerals, see Table 3.4 below (US NAS 1981).

Table 3.4 Longevity and corresponding Mg and hydrogen carbonate levels in drinking water in areas of high and low longevity in the USA (US NAS 1981)

Mineral in drinking water	High longevity area	Low longevity area
Mg, mg/L	20 (average)	5 (average)
Hydrogen carbonate, mg/L	245 (average)	45 (average)

Table 3.5 Macronutrients in drinking water, in summary

Element	Min (mg/L)	Max (mg/L)	Role in the human body	Special comments	General origin if present in water	Health effects when from water	RDA mg/day	Contribution to daily intake, 2 L consumption, studied Swedish waters
Calcium (Ca)	30	80	Bones, teeth, nervous system, muscle contraction (heart), pH regulation, decrease blood pressure, release of hormones, inhibit fat absorption	Antagonistic against Cd, Pb, U; Ca in water is mirrored in hair	Bedrock (e.g. limestone, coral reefs, volcanic material areas)	Decreased frequency of cardiovascular diseases, osteoporosis, cancer. Ca/Mg ratio important (2–3:1). Positive health effects level out extremely high levels.	800–1000	Well water: 0.4–33% Bottled water: 2.7–77%
Magnesium (Mg)	10	50	Muscles (heart), diabetes, increased longevity, carbohydrate metabolism, bones, nervous system, energy	Antagonistic against especially Fe	Bedrock (e.g. limestone, coral reefs, volcanic material areas)	Decreased frequency of cardiovascular diseases, osteoporosis, cancer, diabetes, increased longevity, Ca/Mg ratio important (2–3:1).	300–420	Well water: 0.3–4.2% Bottled water: 0.2–62%
Bicarbonate (HCO3)	100	300	Neutralization of acids, the body's most important buffer		Bedrock (e.g. limestone, coral reefs, volcanic material areas)	Counteracts metabolic acidosis, decreased urinary loss of Ca and Mg, and irritated mucous and intestines, reduces total cholesterol, increased longevity.	Daily intake: n.e.	

(continued)

Table 3.5 (continued)

Element	Min (mg/L)	Max (mg/L)	Role in the human body	Special comments	General origin if present in water	Health effects when from water	RDA mg/day	Contribution to daily intake, 2 L consumption, studied Swedish waters
Sulphate (SO4)	25	100	For longevity and detoxification, in proteins, cartilage, bone, tendons and blood vessels	Concentrations of Mg + SO4 should not exceed 400 mg/L (diarrhoea)	Bedrock (e.g. limestone, coral reefs, volcanic material areas), contamination	Antagonizes heavy metals, regarded active against constipation, high concentrations may cause diarrhoea, accustoming may occur	Daily intake: around 500	
Potassium (K)	10	30	Water balance, nerve signals muscle control, maintenance of blood pressure, 95% of the body's K is located inside cells	Elevated concentrations can cause taste (>10 mg/L)	Bedrock	Not known, water is generally not a source, (KMnO4 for reduction of Fe/Mn may cause elevated levels)	Daily intake: 3500	Well water: 0–2.2% Bottled water: 0–13%
Sodium (Na)	20	70	Electrolyte, nerve signals, balance of body fluids, concentration higher in extracellular fluid, too much induces elevated blood pressure		Bedrock, salt (seawater intrusion), softening filter	Water softeners can give levels of over 300 mg/L, may cause elevated blood pressure.	n.e. Daily intake: 2000–3000	Well water: 0.1–10% Bottled water: 0.1–65%
Chloride (Cl)	20–50 mg/L	250 mg (taste, no health based g.v.)	Most in the extracellular fluid, needed for HCl production, in collagen and connective tissue	Intake of Cl pursues the Na intake, >250 mg/L gives taste	Seawater intrusion, road salt, bedrock, industrial effluents	Corrosion, dissolution of pipe material (e.g. Cu, Pb) at >100 mg/L.	Recommended daily intake <3 g	Well water: 0.3–11% Bottled: 0.03–11%
TDS	100	500						

No health-based guideline value has been proposed or regulatory established on the WHO or EU levels (WHO 2017; EU 1998).

Suggested range Risk-reducing HCO_3 range appears to be 100–300 mg/L. Together with high Ca, SO_4 and other ions TDS should not exceed 1 g/L as an upper limit, and < 500 mg/L is recommended. A suggested lower limit is 100 mg/L.

3.2.5 Potassium (K)

Function in the body, excess/deficiency Potassium, K, is actively involved together with Na in maintaining the body's water balance, physiological nerve function, muscle control and maintenance of blood pressure (Dimitrov and Dimitrov 2012). Ninety-five percent of the body's K is located inside cells. The primary source of K for the general population is their diet, as K is found in all foods, particularly dairy products, meat, vegetables and fruits (MCHL 2011). Daily intake for adults is 2–4 g/day. Both deficient and excess circulating K can lead to disorders in cardiac, muscle and neurological function (Anderson et al. 2010). Diets high in K and low in Na may protect against hypertension (Bowman and Russell 2006).

From drinking water The level of K found in drinking water is low, and not a concern for healthy humans (WHO 2009). Potassium concentrations are generally 0.1–10 mg/L (Aastrup et al. 1995). Potassium chloride (KCl) is sometimes used as an alternative to Na chloride (NaCl) in water softener regeneration, resulting in elevated drinking water concentrations of K. Moderately elevated K concentrations, in general <10 mg/L, may also result from treatment with potassium permanganate, $KMnO_4$, as an oxidant in water treatment to reduce Fe and Mn concentrations (WHO 2017). No health-based guideline value has been proposed (WHO 2017; EU 1998).

Suggested range Risk-reducing K range is hard to set.

3.2.6 Sodium (Na)

Function in the body, excess/deficiency Na is vital together with K for the balance of body fluids and pH level, and Na concentration is higher in the extracellular fluid. In the typical US diet (1994–96), the content of Na was 2–8 g/day, average 3.3 g/day. 500 mg/day is regarded as a minimum for a healthy life (7). Earlier western diets contained lower Na when compared to K. Excess Na in the extracellular fluid can cause elevated blood pressure, while Na deficiency may give symptoms like nausea, lassitude and muscle cramps. Acute effects of excess Na may include nausea, vomiting, convulsions, muscular twitching and rigidity, and cerebral and pulmonary oedema. Sweat loss, if not replaced, reduces both water volume and electrolyte content (Bowman and Russell 2006).

From drinking water Most water supplies contain less than 20 mg/L of Na, but levels can exceed 250 mg/L, due to saline intrusion, mineral deposits, sewage effluents, or salt used in road de-icing. Domestic or private water softeners can provide levels of over 300 mg/L (Gopal 1988). Elevated Na concentrations in drinking water may cause elevated blood pressure (Du et al. 2002; Calabrese and Tuthill 1981). Dietary salt provides all the required Na for most persons. Hence the body generally does not depend upon water for Na. No health-based guideline value has been proposed (WHO 2017; EU 1998). Na concentrations exceeding 200 mg/L may affect the taste of drinking water (WHO 2017). The EU parametric value is 200 mg/L (EU 1998) also due to taste reasons.

Suggested range Risk-reducing Na range appears to be 20–70 mg/L, Na:K, desired ratio of 2–5:1.

3.2.7 Sulphate (SO_4)

Function in the body, excess/deficiency Inorganic sulphate, SO_4, is required for the synthesis of 3′-phosphoadenosine-5′-phosphosulphate (PAPS), which in turn is required for synthesis of many compounds, including chondroitin in cartilage, bone, tendons and blood vessels; taurine (found throughout the body as a conjugate of bile acid); heparin (a blood coagulant); and in proteins (FNB 2005). Average daily intake of SO_4 from drinking water and food is approximately 500 mg/day, with food generally being considered to be the major source of sulphate; biodegradation of proteins containing the sulphur amino acids methionine and cysteine occurs routinely (FNB 2005).

From drinking water Naturally available drinking water may contain sulphate in a range of 10–500 mg/L or higher. Concentrations up to 5000 mg/L have been reported (Aastrup et al. 1995). Sulphur is known to antagonize heavy metals, and SO_4 in drinking water is considered to decrease health risks connected to the intake of heavy metals (Watts 1997). High concentrations in drinking water can substantially contribute to daily intake, and levels above 1000–1200 mg/L can be laxative, especially in infants fed formula prepared with high sulphate water (WHO 2017). Low drinking water sulphate may contribute to constipation, since especially SO_4 from $MgSO_4$ tends to bind water in the intestines, making the content more fluid (Bergmark 1959). However, intake of fibres is necessary to maintain the consistency of the intestinal contents. People regularly drinking water with low SO_4 and Mg concentrations may experience more pronounced laxative effects during an initial period of a few weeks when such people change to high sulphate water. The death rates due to high blood pressure and arteriosclerosis were higher in cities where the drinking water had low concentrations of Ca, Mg, Na, K, Ba and SO_4 (Schroeder 1966).

In Sweden, concentrations of $SO_4 > 100$ mg/L are regarded "suitable with annotation" and may be corrosive (NSFA 2001). When Mg fortification of drinking water is practiced, an upper limit of sulphate may have to be revised depending on experience, since the laxative effects of $MgSO_4$ are well known (Izzo et al. 1996). Since SO_4 is important for human health, a lowest acceptable limit may be needed in the end. However, there are no studies on this topic, which is why a lower limit is hard to establish. High concentrations give rise to a certain taste, and it is generally considered that taste impairment is minimal at levels below 250 mg/L (WHO 2017). No health-based guideline value has been established (WHO 2017; EU 1998). The EU parametric value for SO_4 is 250 mg/L (EU 1998).

Suggested range The risk-reducing SO_4 range appears to be between 25–100 mg/L. Due to recommended level of all minerals, TDS < 500 mg/L, sulphate should be around 50 mg/L; however, concentration up to 100 mg/L do not represent any harm, but rather positive effects. For Mg-fortified water, a tentative upper limit is recommended to be (Mg + SO4) ≈ 250 mg/L, with maximum Mg concentration of 150 mg/L. Together with high Ca, SO_4 and other ions TDS should not exceed 1 g/L as an upper limit, and < 500 mg/L is recommended. A suggested lower limit for TDS is 100 mg/L.

3.2.8 Chloride (Cl)

Function in the body The majority of Cl in the body (about 70%) is distributed in the extracellular fluid, while much of the remaining Cl is localized in the collagen of connective tissue, and Cl is needed for production of hydrochloric acid (HCl) in the stomach (Bowman and Russell 2006). Chloride content in the normal adult human is about 82 g. On the basis of an obligatory loss of approximately 530 mg/day, a dietary intake for adults around 1 g of salt is needed per day. The daily intake should be <3 g. Intake of Cl often follows the Na intake (NaCl) (NSFA 1997).

Deficiency Hypochloraemic alkalosis was diagnosed in a breast-fed baby after severe vomiting and dehydration (Hill and Bowie 1983), and anorexia and failure to thrive are reported in chloride-deficient infants (Grossman et al. 1980).

Excess In experimental animals, hypertension has been associated with high NaCl intake, most probably related to Na content rather than Cl (Dep of Nat Health and Welfare, Canada 1978). A dose of 1 g of NaCl per kg of bodyweight was reported to have been lethal in a 9-week-old child (EURO Rep. and Stud. 1978). There are four older Russian studies, both animal and epidemiological, from the 1960s and 1970s indicating various negative health effects relating to consumption of water with high levels of chloride (up to 2500 mg/L), however, as these waters had at the same time higher levels of sodium or total dissolved solids, it was not possible to distinguish if it was a real pure effect of chloride or other elements, either individually or in total.

From drinking water In general, the concentration of Cl in drinking water ranges from 30–70 mg/L. Chloride levels in unpolluted waters are often below 10 mg/L and sometimes below 1 mg/L (Dep of Nat Health and Welfare, Canada 1978). Evidence of a general increase in chloride concentrations in groundwater and drinking water has been found (EURO Rep. and Stud. 1978), but exceptions have also been reported (Gelb and Anderson 1981). Water treatment processes such as chlorination or the use of $FeCl_3$ to decrease levels of Fe(II) also increases Cl concentration a little. Elevated chloride in drinking water often originates from run-off containing road de-icing salts or seawater intrusion in coastal areas (Dep of Nat Health and Welfare, Canada 1978). In the USA, aquifers prone to seawater intrusion have been found to contain chloride at concentrations ranging from 5 to 460 mg/L (Phelan 1987). Salt in the diet generally provides an adequate amount of Cl required for the body and hence there is often no need for salt from one's drinking water. Excess chloride in water increases corrosion of pipes, as soluble metal chlorides are formed (EURO Rep. and Stud. 1978). Cl concentrations exceeding 100 mg/L are regarded as "suitable with annotation", due to corrosion risk (NSFA 2001). The taste threshold of Cl in water is 200–300 mg/L. The taste of coffee is affected if the concentration of Cl as NaCl is 400 mg/l and as $CaCl_2$ is 530 mg/L. The World Health Organization (WHO 2017) and EU (1998) have defined a recommended upper limit of 250 mg/L for Cl due primarily to the impact on the taste of water and corrosion.

Suggested range Risk-reducing Cl range appears to be 20–50 mg/L.

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Chapter 4
Micro-minerals at Optimum Concentrations – Protection Against Diseases

Ingegerd Rosborg, Margherita Ferrante, and Vasant Soni

Abstract Micro-minerals are as necessary as macro-minerals, but in lower doses, micro-doses. Drinking water may be a substantial source. Goitre is uncommon where iodine (I) is >50 μg/L. Levels of about 1 mg/L of fluoride (F) in drinking water is protective against dental caries, but more than 1.5 mg/L may cause dental stains or in the worst case bone deformations. Low selenium (Se) and molybdenum (Mo) is connected to heart diseases and cancer. Lithium (Li) in drinking water decreases the incidence of violent crimes and suicide. Boron (B, <1 mg/L) and chromium (Cr-III) from drinking water may be beneficial. Copper (Cu) and iron (Fe) are nutrients, but concentrations >1 mg/L may cause diarrhoea and subsequent symptoms. Elevated manganese (Mn) may negatively affect the nervous system.

4.1 Introduction to Trace Elements

The daily need for micro-elements is in the order of μg/day, while macro-elements are needed in mg/day doses, and deficiency in micro-elements may be as harmful as deficiencies from macro constituents. Concentrations in drinking water may be in the order of the daily requirement for the respective elements in specific waters. Approximately 20 mineral elements are regarded as essential for humans: Ca, Na, K, Cl, Mg, Fe, Zn, Cu, Cr, I, Co, Mo, P, S, Se and Zn are unequivocally essential for human health. A second group of elements that have beneficial health effects,

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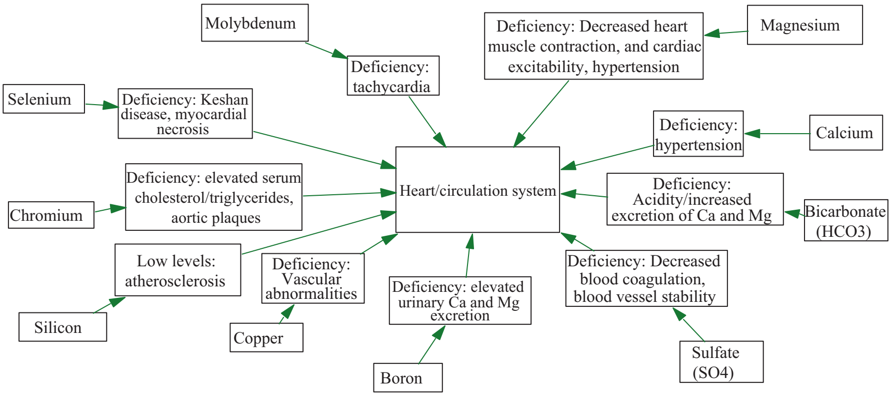

Fig. 4.1 The influence of some macro- and micro-elements on heart function (Rosborg 2005)

include F in the prevention of dental caries and B, Mn, Ni, Si and V, which may be considered essential for humans (WHO 2005; Bowman and Russell 2006). The scientific proof for some of the elements is still under consideration. These essential minerals may be contained naturally in water (Se, F, Zn, Mo, Cr, Fe, I etc) or through intentional (F) or incidental (such as Cu leaching from piping) addition in drinking water supplies (Rosborg 2005).

In the monograph *Nutrients in Drinking Water* (WHO 2005), drinking water as a source of minerals is discussed especially for F and Mg, and partly also Ca. Regarding micro-elements, the risk of having too much is discussed for water with elevated concentrations used for preparation of infant formula. This accounts for Mn, Mo, Cu, Fe, Zn or Na. However, especially some studies in Russia add interesting information. In these studies, a large number of elements and ions were analysed in connection with investigations of health differences between areas with different bedrocks and groundwater qualities (Lutai 1992; Muzalevskaya et al. 1993).

Mg in connection with cardiovascular diseases has dominated the discussion about the need for minerals from drinking water. To expand the discussion to more minerals, their potential influence on the heart and circulation is presented in Fig. 4.1.

4.2 TRACE Elements in Alphabetic Order

4.2.1 Boron (B)

Function in the body B is introduced to the environment by volatilization of boric acid in thermal processes or by anthropogenic activities (International Programme on Chemical Safety, IPCS 1999; Bustos et al. 2008). B is an essential element and participates in calcium, phosphorus and magnesium absorption in bones and joints, and helps control inflammatory processes in humans (Hunt and Idso 1999; Usuda et al. 2007; McCoy et al. 1994, b; Newnham 1994). B is also a modulator in immune response, and is important for both brain composition and function, as its deficiency is connected to depressed psychomotor skills, cognitive performance, depressed attention, perception and memory (Penland 1998; Goldbach et al. 2001). Common intake is 1–13 mg/day (Bowman and Russell 2006), while Rainey and Nyqvist (1998) report 0.89–2.12 mg/day. B intakes should be >1.0 mg/day (Nielsen and Meacham 2011). Beneficial actions of B include arthritis alleviation or risk reduction, bone growth and maintenance, central nervous system function, cancer risk reduction, hormone facilitation, immune response, inflammation reduction, and oxidative stress modulation (Nielsen and Meacham 2011). Investigations on animals also show that B is essential for eyes for adequate vision (Eckhert and Rowe 1999; Fort et al. 1999).

Deficiency Patients suffering from arthritis and osteoporosis successfully treated with 1–3 mg B per day have recovered or showed less symptoms (Newnham 2002).

Excess When administering high doses of boron of up to 80 mg/kg/day in animal models adverse effects such as anorexia, weight loss, bone disorders and testicular atrophy have been observed, specially in mice (Price et al. 1996; Korkmaz et al. 2006). The average dose of boric acid to produce toxic symptoms, mostly represented by vomiting, diarrhoea and abdominal pain, is presumably in the range of 100 mg to 55.5 g (Litovitz et al. 1988).

From drinking water Concentrations of B in groundwater throughout the world range widely from <0.3 to >100 mg/l (Butterwick et al. 1989). In general, in Europe the greatest B concentrations are in the south. There are several reports describing adverse effects of high B intake from drinking water on animal reproduction (WHO 2005). In a study in northern Argentina, drinking water boron ranged 377–10,929 μg/L. Serum boron concentrations during pregnancy were correlated strongly with whole-blood and urinary boron, and, to a lesser extent, with water boron (Igra et al. 2016). Arthritis is less frequent in regions where drinking water B concentrations are high. In New Zealand, there were spas that were noted as being able to help people to overcome arthritis. Some of the hot springs contained between 20 to 80 μg/L of B (Newnham 2002). There is a tendency towards a beneficial effect with low-dose environmental exposure (less than 1 mg/L of B) in drinking water, as birth rate was higher and premature mortality rate was lower in municipalities with significant B concentration in drinking water (albeit lower than 1 mg/L) (Yazbeck et al. 2005). In addition, the Kashin-Beck disease, an endemic disease in parts of China, is connected with low hair B levels (Peng et al. 2000). Boron concentrations in drinking water were mirrored in urine (Cortes et al. 2011), and in foetus. Boron is present in seawater at levels up to around 6 mg/L, that is why RO water generally is additionally treated with ion-exchange filter to reduce the concentration of B (Withers 2018). The EU standard for boron in drinking water is 1 mg/L (EU 1998). The WHO guideline value is 2.4 mg/L (WHO 2017).

Suggested range Risk-reducing B range appears to be 0.1–1 mg/L.

4.2.1.1 Chromium Cr (III)

Function in the body Trivalent chromium is essential to normal carbohydrate, lipid and protein metabolism, and hence for the control of diabetes (Anderson 1998; Anderson 1999; Dattilo 2003). Cr is present in the body in GTF, Glucose Tolerance Factor, a hormone excreted with insulin. GTF is needed when insulin is attached to, e.g. muscle cells. The median intake is 50 μg/day, about 35 μg/day is regarded as Adequate Intake, AI, (NAP 2001).

Deficiency Serum Cr deficiency is associated with total cholesterol and triglyceride concentrations in candidates for bariatric surgery (Lima et al. 2014). Possibly low Cr, as detected in toenail concentrations, may be related to heart disease (Rimm 2002; Simonoff 1984).

Excess Oxalates and high Fe intake decrease Cr bioavailability (WHO 1996a). Articles reporting health changes due to elevated Cr (III) were not available.

From drinking water Cr (III) content of drinking water is generally very low due to limited sources and limited solubility 0.5–2 μg/L. In groundwater in the USA, Cr (III) levels up to 50 μg/L have been reported. Food in general only contributes approximately 50 μg/day and potentially water may provide a substantial contribution to daily intake. Cr (III) from drinking water is poorly absorbed. Drinking water may also contain toxic hexavalent, Cr (VI), either naturally or from contaminations by industries (WHO 2017). Some people who use water containing Cr (III) in excess of the drinking water standard over many years could experience allergic dermatitis and skin reactions (US EPA 2012b). EU parametric value and WHO provisional guideline value is given only for total Cr: 50 μg/L (WHO 2017; EU 1998).

Suggested range Risk-reducing Cr^{3+}, Cr (III), range appears to be 0.01–0.05 mg/L, while Cr (VI) kept as low as possible.

4.2.2 Chromium Cr (VI)

The hexavalent compounds are the most toxic. Chromium (VI) can induce carcinogenesis because of its ability to cross biological membranes easily and react with protein components and nucleic acids inside the cell (Sun and Liang 2008). Typical Cr(VI)-containing waters have a $pH > 7.5$ and Ca concentration < 50 mg/L. Contact with ultramafic rocks activates Cr(VI) formation by a catalytic mechanism. The highest Cr(VI) values were observed in shallow porous aquifers downstream of ophiolites (Kaprara et al. 2015). A Greek study showed that drinking water contaminated with Cr(VI) was a cause of cancer, especially liver, lung, kidney, and genitourinary organs among women (Linos et al. 2011). Guideline value is 0.05 mg/L, total Cr (WHO 2017; EU 1998).

Suggested range Risk-reducing Cr^{6+}, Cr(VI), range for total Cr appears to be <0.05 µg/L.

4.2.3 Cobalt (Co)

Function in the body Some types of bacteria in the human digestive tract synthesize vitamin B-12, which contains Co (Albert et al. 1980). Homocysteine, a harmful substance for the heart may be controlled by vitamin B-12 (Deshmukh 2010). Co may increase the oxygen-carrying capacity of the blood which is helpful under conditions of ischemia and tissue hypoxia. There is a competition between Co and Ca for intracellular Ca-binding proteins (Simonsen et al. 2012). The total daily intake of Co is variable, but generally on the order of µg/day (Simonsen et al. 2012).

Deficiency Vitamin B-12 deficiency is manifested by degeneration of the spinal cord, lesions in one's nervous system and painful pricking sensation and numbness of extremities (Bowman and Russell 2006).

Excess Adverse effects of high Co intake may include impacts on the thyroid gland, the lungs (cobalt asthma, and hard-metal disease), the skin (allergic contact dermatitis) and the immune system, and may include a possible carcinogenic potential. Toxic levels appear to be in order of mg/day (NSFA 2015).

From drinking water Studies on the influence on the human body of Co from drinking water were not available. Co in European bottled waters is generally below the detection limit, 0.002 µg/L (Reimann and Birke 2010). Well waters in southern Sweden had Co concentration in the range of <0 –14 µg/L (Rosborg et al. 2002). No standards for Co content in drinking water have been prescribed (WHO 2017; EU 1998).

Suggested range Risk-reducing Co range is difficult to set, but a suggestion is 0.005–0.02 mg/L, while Cr(VI) kept as low as possible.

4.2.4 Copper (Cu)

Function in the body Cu is important in energy production, antioxidant function, Fe utilization and possibly cardiovascular health. RDI for adults is 0.9 mg/day (Bowman and Russell 2006), 2 mg/day (WHO 1996a). As an essential mineral Cu is required for adequate growth, cardiovascular integrity, lung elasticity, neovascularisation, neuroendocrine function and Fe metabolism (NAC 2000). The activity of a number of enzymes depends on appropriate Cu levels in the body (Prohaska 2014).

Deficiency Children suffering from Menkes syndrome, with minimal Cu absorption, exhibit mental deterioration, failure to thrive, hypothermia, hypopigmentation, anaemia and connective tissue abnormalities (Harris and Gitlin 1996). Hypochromic anaemia and adult onset peripheral neuropathy/ataxia are the two most common clinical features of copper deficiency (Prohaska 2014). Elevated Zn, Fe and Mo decrease Cu bioavailability (WHO 1996a). Fe, Zn and Cu interact with each other, and the respective ratios are important for proper health (Nacagawa et al. 2014; Gupta et al. 2012; Willis et al. 2005).

Excess Wilson's disease is a toxicity disorder, where Cu accumulates in the liver, brain and eyes, and ends in hepatic cirrhosis and neurological degeneration (WHO 1996a).

From drinking water Cu concentrations in surface waters ranged from 0.0005 to 1 mg/L in several studies in the USA, but levels can be >30 mg/L, due to corrosion of interior copper plumbing (WHO 2017). Low-mineralized, softened water or acid water readily dissolves Cu from pipes. NOM, Natural Organic Matter, in combination with hard water is also a cause of Cu corrosion from pipes (Korshin et al. 1996; Holmström and Swedling 1997). High copper content in the water can be seen as the turquoise deposits in sanitary ware. Elevated Cu levels may cause intestinal problems, such as, diarrhoea, especially in infants fed formula prepared with such water (Rosborg 2005; Knobeloch et al. 1994; Stenhammar 1999), which may also be caused by an anti-microbial effect in the intestines (Grimsdottir and Hensten-Pettersen 1993). Copper sulphate, $CuSO_4$, is a gastric irritant and has been used as a vomiting agent (Davis et al. 1986). In fully flushed water pipes, Cu concentrations tends to be low. At levels around 2.5 mg/L, copper imparts an undesirable bitter taste to water (WHO 2004). Phosphate has been used to decrease Cu corrosion on pipes (WHO 2017). The EU (1998) and WHO (2017) guideline values are 2 mg/L, with the comment that the standard will prevent staining. The US EPA (2012b) standard is 1.3 mg/L for health reasons. The National Swedish Food Administration, NSFA, has 0.2 mg/L "suitable with annotation" for aesthetical reasons, since there is risk for discolouration of water, turquoise (NSFA 2001) (Fig. 4.2).

Suggested range Risk-reducing range for Cu concentration appears to be 0.02–0.2 mg/L.

4.2.5 Fluoride (F)

Function in the body F is classified as a trace element and possibly an essential trace element, being recognized as beneficial in the prevention of dental caries (tooth decay) when ingested in amounts of approximately 0.05 mg/kg body weight per day and applied typically with dental products, such as toothpaste (EFSA 2005) (Fig. 4.3). It also affects bones, the thyroid gland (Liu et al. 2014; WHO 2010) and

Fig. 4.2 Green precipitates of copper from copper pipes in a public sauna, Värmdö, Sweden (Frejing 2012)

Fig. 4.3 Fluorosis, stains on teeth due to elevated fluoride in drinking water (Limeback 2014)

blood sugar levels (EFSA 2005). The WHO (1996a) states that the daily intake may be 0.2–2 mg/day, or higher if the drinking water levels are elevated. RDA is 3–4 mg/day (Bowman and Russell 2006). Studies on mice have shown that F improves Fe absorption (Bowman and Russell 2006).

Deficiency Dental enamel which contains F is less likely to develop caries, because of greater resistance to ingested acids or to acids generated from ingested sugars by bacteria in the mouth. Fluoride also has been shown to inhibit sugar metabolism by oral bacteria (EFSA 2005), and stated to be needed for proper bone formation (Anonymous 2005).

Excess Fluoride toxicity includes cosmetic effects on teeth and potential bone deformities. Neurotoxicity, carcinogenicity, developmental and reproductive toxicity, allergies and increased risk of bone fracture are not clear or sufficiently confirmed (EFSA 2005).

From drinking water Natural content of F in drinking water is generally less than 0.5 mg/L, but may be up to 100 mg/L in some groundwaters in Africa, India and other parts of the world (NSFA 1989). Its absorption from drinking water is almost 100% (Bowman and Russell 2006). Concentrations of F between 0.8 mg/L and 1.2 mg/L were regarded as protective against dental caries in Sweden (NSFA 1989), the USA and other countries. This concentration is fully protective against skeletal fluorosis, but not against mild forms of dental fluorosis (depending on exposure from other sources). Mild forms of dental fluorosis have been found in communities supplied with drinking water containing fluoride above 1 mg/L (EFSA 2005). Studies have shown that the likelihood of developing dental fluorosis is 4.4 times higher in regions with high water F content 1.5–2.0 mg/L (Fawell et al. 2006; Indermitte et al. 2009; Alarcon-Herrera et al. 2001; Fallico et al. 1984) than in areas with F concentrations lower than the health-based guideline standard of 1.5 mg/L. Endemic fluorosis induced by high concentrations of fluoride in water and soils is a major health problem in several countries, particularly in volcanic areas. From studies of the Herculaneum victims of the 79 AD eruption, it was stated that they suffered from endemic fluorosis (Petrone et al. 2010). Excess F in drinking water is also suspected for neurological toxic effect, as students in three areas were examined orally: one low concentration area with F 0.6 mg/L, one median with 1.70 mg/L and one high with 4.99 mg/L of F in the drinking water. In the low F area there were no subjects that had below average IQ, in the median 13.3%, while in the high 46.7% of the students had IQ below average (Razdan et al. 2017). Since the 1950s, F has been added to public water supplies to prevent dental caries in some countries (WHO 2005). To avoid the risk with dental fluorosis in communities receiving fluoridated water, not more than 0.7 mg/L has been recently suggested in the USA (US HHSD 2011). However, calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is the main constituent of both the enamel and the dentin, situated underneath the enamel, and is also prone to attack by acids at low pH in the saliva (Lindström Claesson 2009). Thus, a large study in Denmark proved that Ca: 170 mg/L had the same anti-dental caries effects as F: 1 mg/L in drinking water. The authors recommend optimum content of Ca (40–50 mg/L) and F (0.75 mg/L) in drinking water to control dental caries (Bruvo et al. 2008). Even high pH in drinking water damages your teeth (Lindström Claesson 2009). The WHO and EU guideline value is 1.5 mg/L (WHO 2017; EU 1998).

Suggested range Risk-reducing F concentration appears to be approximately 0.5–1.0 mg/L.

4.2.6 Iodide (I)

Function in the body Iodide is needed for thyroid hormones, which regulate carbohydrate and fat metabolism, reproductive function and growth and development (Bowman and Russell 2006). The current World Health Organization recommendation for iodide intake is between 150 and 300 µg/day (ETA 1985). WHO (2017) has the value 80–150 µg/day.

Deficiency Deficiency causes goitre and mental retardation. Salt iodization began in the 1920s in the USA in response to the prevalence of goitres in certain populations in iodine-deficient areas (Meletis 2011). However, dietary salt restriction is recommended as a first-line therapy for the 74.5 million people in the USA with hypertension. This causes lower iodide intake through iodized table salt. Data suggest that 25% of vegetarians and 80% of vegans are iodine deficient (Krajcovicova-Kudlackova et al. 2003). In addition, the other halogen elements, fluoride, chloride and bromide, are similar to iodide in structure and compete for uptake and utilization, and especially excess fluoride from dental treatments increase the incidence of thyroid diseases (Meletis 2011).

Excess Long-term symptoms of excess iodide are weight loss, tachycardia, muscle weakness and skin warmth. If there is underlying heart disease, excess iodine may be lethal (Bowman and Russell 2006). Excess Iodine may cause apoptosis in the thyroid gland in Hashimoto thyroiditis disease (Xu et al. 2016).

From drinking water The mean concentration of total iodide in drinking water in the USA is 4 μg/L, with maximum reported value; 18 μg/L (NAS 1980). In an area of Sri Lanka where goitre was uncommon, iodide concentrations were 84 μg/L in drinking water (Fordyce et al. 2000), and 50 μg/L in public drinking water was considered adequate to avoid goitre (Oberlin et al. 2006). In a study in China, iodine -induced goitre prevalence was 6.3% in areas with drinking water where the iodide levels were 150–300 μg/l and 11.0% in the areas with >300 μg/l (Shena et al. 2011). Between 2003 and 2010, the use of thyroid disease medication among Israeli adults increased from 2.9% to 4.7%, and during this time a large number of seawater reverse osmosis desalination plants were built along Israel's coast, elimination almost 100% of iodine from drinking water. The Ashkelon desalination plant is the major source of drinking water in the Ashkelon District. Thus, researchers obtained data on iodine status in adults in the Ashkelon district without reported or known thyroid disease. Results showed possible iodine deficiency (Tg ≥ 10 μIU/mL) among 76% of the participants, which was higher than that reported a decade ago (Ovadia et al. 2013). High iodide concentrations in drinking water has recently also been proven to cause detrimental effects on children intelligence (Liu et al. 2008). A study on refugees in a camp in the Algerian desert where the average iodide concentration in water was 108 μg/L showed that children were suffering from iodine-induced goitre (Henjum et al. 2010). There are several reports of iodination of village water supplies in China to reduce endemic goitre and to kill most microorganisms (Maberley et al. 1981). No guideline value has been established (WHO 2017; EU 1998).

Suggested range Risk-reducing iodide range is difficult to set, but appears to be 0.005–0.05 mg/L.

4.2.7 Iron Fe(II)

Function in the body Fe, as Fe^{2+}, is essential for human health, but is also toxic. It is included especially in haemoglobin, which transports oxygen to the cells, but also in, e.g., myoglobin, a storage protein of Fe inside cells. The adult human body requires about 15 mg/day of Fe (Bowman and Russell 2006). Absorption takes place in the small intestines, and excretion is extremely low. Cu is involved in Fe utilization. Zn, Mo and Cu are antagonistic with respect to Fe, and they all act antagonistically towards one another (WHO 1996a).

Deficiency Symptoms of iron deficiency anaemia include fatigue and muscle weakness, hypotension, headache, palpitation, fainting, dyspnoea, angina pectoris, neuropathy, restless legs and emaciation (Bowman and Russell 2006).

Excess Excessive ingested Fe can cause excessive levels in the blood, since cells in the gastrointestinal tract have been damaged by the Fe, and regulation of absorption is prevented (El-Harbawi et al. 2010). Intestinal disturbances like diarrhoea, lethargy, abdominal pain, metabolic acidosis and liver damage may occur (Banner Jr and Tong 1986; Klaassen et al. 1996; Rosborg 2014). The mechanism of toxicity to tissues in the body is thought to begin with acute mucosal cell damage (Laine et al. 1988), as a direct oxidative effect of Fe. This may lead to severe haemorrhagic necrosis and the development of shock. Hemochromatosis is a hereditary disease, which generally is diagnosed on men. Their Fe uptake is up to ten times higher than normal. Sullivan (1981, 2007) proposed that their elevated Fe levels play major role in producing atherosclerosis. His major basis for this proposal was that menstruating women have a reduced Fe load, and thereby strong protection against atherosclerosis, compared to men of the same age. On the same basis Ong and Halliwell (2004) suggest that Fe can be involved in Alzheimer's disease.

From drinking water Fe appears as Fe^{2+} in drinking water. However, in contact with air or with the presence of ferruginous bacteria it becomes oxidized: $Fe^{2+} \rightarrow Fe^{3+}$, and forms rusty red coloured deposits in pipes and installations, on bathtubs and wash-basins, as well as rusty colouring on clothes (Fig. 4.4). Thus, Fe is often eliminated by deposition in filters after oxidation with air, $KMnO_4$, or chlorine. Fe intake can be measured in hair samples from individuals who drink water containing Fe (Rosborg et al. 2003). Cattle, especially calves, can suffer from ample and bloody diarrhoea, followed by loss of appetite and weight, apathy, paralysis and finally death at elevated Fe concentrations in the water used for preparation of milk after suckling. Autopsy of three calves on a farm in southernmost Sweden, who had died after severe diarrhoea, weight loss and apathy, showed more or less inflamed gastric tract. Hair analyses of horses and men experiencing weight loss, diarrhoea, and additional symptoms showed elevated Fe levels mirroring levels in their drinking water (Rosborg 2014). From these studies it seems like there is no health threat at levels below 1 mg/L. However, more studies are needed. In a population-based

Fig. 4.4 Rusty deposits in a bathtub (ISEA 2014)

cohort recruited in south-eastern Norway and a registry of water quality derived from Norwegian waterworks, iron, aluminium, acidity (pH), colour, turbidity and coliform bacteria were studied. The risk of developing inflammatory bowel disease, including ulcerative colitis and Crohn's disease, was associated only with high iron content, as it increased by 21% when the iron content in drinking water increased by 0.1 mg/L. An attempt to explain the finding is that high iron concentration works as a catalyst for oxidative stress, which will cause inflammation and/or increase the rate of cell mutations, and stimulates the growth of bacteria and increases the likelihood of inappropriate immune responses in genetically predisposed individuals (Aamodt et al. 2008). In this study, the highest Fe concentration was 0.39 mg/L, which was regarded safe in the Swedish study, thus questioning 1 mg/L as a safe upper limit. In *Nutrients in Drinking Water* (WHO 2005), Fe is not listed as a potential cause of diarrhoea, and WHO (2017) states that a value of approximately 2.5 mg/L does not present a health hazard. The National Swedish Food Administration (NSFA 2001) guideline value is 0.2 mg/L, aesthetic. There is no health-based guideline value (WHO 2017; EU 1998), but the EU (1998) parametric value for aesthetic reasons, colour of water, is 0.2 mg/L, WHO (2017) guideline is 0.3 mg/L, with the comment: "Levels likely to give rise to consumer complaints". "Sanitary security" limit is 2 mg/L (Davison et al. 2005).

Suggested range Risk-reducing Fe range appears to be 0.02–0.2 mg/L.

4.2.8 Lithium (Li)

Function in the body, excess Daily intake is normally 0.2–0.6 mg, while pharmacological intake is some 100 mg/day (Bowman and Russell 2006).

Deficiency In clinical practice Li is widely used for the treatment of bipolar disorder, and for preventing suicidal behaviour in people with mood disorders. Li has potential clinical implications in the prevention of Alzheimer's disease (Forlenza et al. 2011), and a lower incidence of dementia in bipolar patients treated with Li has been reported at 0.3 mg/day (Nunes et al. 2013).

Excess Li treatment of rats has been shown to lower the uptake and turnover of iodine (Hullin and Johnson 1970). Excess Li in the treatment of humans may cause transient nausea, abdominal discomfort, loosening of stools, thirst, increased frequency of urination, muscular weakness, fine tremor of hands, fatigue and lethargy (Gershon and Shopsin 1973). Chronic lithium treatment is associated with weight gain and hypothyroidism (Grandjean and Aubry 2009).

From drinking water Low levels of Li in drinking water are approximately 0–10 µg/L with median concentrations of 12–60 µg/L and 70–160 µg/L on the high end of the range. Mineral water from Poland may have 400–700 µg/L and levels as high as 10 mg/L has been reported in bottled water from Slovakia (Reimann and Birke 2010). Sociological factors play an important role in suicide, but regions with higher natural Li concentrations in drinking water are associated with lower suicide mortality rates (Kapusta et al. 2011; Ohgami et al. 2009), and an increase in Li concentration in drinking water by 0.01 mg/l was associated with a decrease in the suicide rate of 1.4 per 100,000 (Kapusta et al. 2011). Mean suicide rates in 27 Texas counties over a 10-year period were consistently lower in those with "high" natural lithium concentrations in drinking water (70–160 µg/l) than in counties with "medium" (12–60 µg/l) or "low" (0–10 µg/l) water lithium levels. Thus, using data for 27 Texas counties from 1978–1987, it was shown that the incidence rates of suicide, homicide and rape were significantly higher in counties whose drinking water supplies contain little or no lithium than in counties with water lithium levels ranging from 70–170 µg/L; the differences remained statistically significant after corrections for population density. Incidence rates of robbery, burglary and theft were also lower (Schrauzer and Shrestha 1990). In a recent Danish nationwide, population-based, nested case-control study, patients with dementia were compared with healthy individuals. The incidence rate ratio (IRR) of dementia was decreased in those exposed to more than 15.0 µg/L and 10.1–15.0 µg/L, but increased with 5.1–10.0 µg/L in their drinking water. Similar patterns were found with Alzheimer's disease and vascular dementia as outcomes. However, the researchers comment that confounding from other factors associated with municipality of residence cannot be excluded, which is always the problem with "ecological studies" (Kessing et al. 2017). On the other hand, a study in northern Argentina, the Puna region, indicated that hypothyroidism can be triggered by the ingestion of too much Li via groundwater. The Puna region was selected since earlier studies had shown levels as high as 1005 µg/L in tap water in this area (Concha et al. 2010). However, no water samples were collected in connection with the study and high levels of As, Cs, B and Rb were also present in the drinking water (Broberg et al. 2010). From these studies it appears that concentrations of approximately 100–200 μg/L are optimal, but as low as 10 μg/L appears to be beneficial. There is no guideline value (WHO 2017; EU 1998).

Suggested range Risk-reducing Li range appears to be 0.01–0.1 mg/L.

4.2.9 Manganese Mn (II)

Function in the body Mn is an essential element to humans, and acts as an enzyme co-factor (superoxide dismutase, glutamine synthetase, and arginase). It is important for carbohydrate, amino acids, proteins, lipid and sterol metabolism and oxidative phosphorylation (generating cellular energy-ATP) (WHO 2002; Fraga 2005), and Mn-SOD is an important anti-oxidizing agent. Daily consumption of Mn is in the range 0.7–10.9 mg/day, and can be even higher among vegetarians and heavy tea drinkers (Freeland-Graves et al. 1987; Greger 1999; ATSDR 2000). Safe and adequate intake is set to be 2–5 mg/day in the USA (NRC 2000).

Deficiency Mn deficiency has been associated with osteoporosis, diabetes, epilepsy and other disorders in the brain, atherosclerosis, impaired wound healing, and cataract (Klimis-Tavantzis 1994). Epilepsy subjects are also often deficient in Mg, Zn and Cu, in addition to Mn (Grant 2004).

Excess Symptoms in persons suffering from Mn poisoning are mainly related to the nervous system and brain, and include hyperirritability, hallucinations and violent behaviour and Parkinson-like symptoms (Mena 1981). High Ca intake decreases Mn bioavailability (WHO 1996a). Children exposed to airborne Mn in Molonga mining district in central Mexico had significantly higher median values for hair Mn (12.6 μg/g) and blood Mn (9.5 μg/L) than children not exposed (0.6 μg/g and 8.0 μg/L, respectively). Hair Mn was inversely associated with verbal IQ, performance IQ, and total scale IQ. The findings suggest that airborne Mn environmental exposure is inversely associated with intellectual function in young school-age children (Riojas-Rodríguez et al. 2010).

From drinking water The concentration of Mn in water depends on pH and oxygen concentration, as higher concentrations appear in water with lower pH values and in oxygen-poor waters. Mn usually occurs together with Fe. At concentrations exceeding approximately 100 μg/L, blackish deposits occur especially on irrigated concrete and on clothes (Aastrup et al. 1995; Thuvander and Oskarsson 1997). Bouchard et al. (2011) assessed the relations between exposure to manganese from drinking water and children's intelligence quotient (IQ), and the relations between manganese exposure from water consumption and from the diet with children's hair manganese concentration. The median Mn in children's home tap water was 34 μg/L (range: 1–2700 μg/L). Mn in hair increased with manganese intake from water consumption, but not with dietary Mn intake. Higher Mn in water and hair were significantly associated with lower IQ scores. A ten-fold increase in water Mn was associated with a decrease of 2.4 IQ points. There was a 6.2-point difference in IQ between children in the lowest (1 μg/L) and highest (216 μg/L) water Mn quintiles. The authors concluded that exposure to Mn at levels common in groundwater is associated with intellectual impairment in children. Alterations in Fe status and negative effects on the nervous system may occur from intake of drinking water with elevated Mn concentration, > 600 μg/L (Bouchard et al. 2011). FNB (2001) state that Mn intake can be measured in hair samples from individuals who drink water containing Mn. At levels above 0.1 mg/L, Mn can cause an undesirable taste in beverages, and stains on sanitary ware and laundry (WHO 2017). The EU (1998) parametric value is 0.05 mg/L, and WHO (2017) 0.04 mg/L.

Suggested range Risk-reducing Mn range appears to be 0.005–0.025 mg/L.

4.2.10 Molybdenum (Mo)

Function in the body Mo is an essential element, which is important for detoxification in the liver, and is necessary for metabolism of sulphur amino acids. Sulphite oxidase deficiency or absence leads to neurological symptoms and early death (Abumrad et al. 1981). Mo is needed for Fe mobilization in the liver (Bowman and Russell 2006). The GI absorption is 50–80%. Acidification decreases the soil and well water concentration of Mo (Rosborg et al. 2002). Daily intake was estimated to range between 100 and 500 μg (Friberg and Lener 1986), while the average daily intake in Australian adults is 73–82 μg/day for women and 90–110 μg/day for men (FSANZ 2008). Safe and adequate intake was suggested to be 0.075–0.25 mg/day (NAS 1989), while RDA was set to about 40–50 μg/day (FNB 2001). WHO (2017), on the other hand, states that estimated daily requirement is 0.1–0.3 mg/day.

Deficiency Too high Cu intake may exhibit Mo deficiency symptoms, and Mo deficiency causes Cu overload in animals. Thus, Cu-deficient humans could be at greater risk of Mo toxicity (Bowman and Russell 2006). Mo status may influence susceptibility to some forms of cancer, especially oesophageal (Burrell et al. 1966), and Mo deficiency was connected to myocardial effects of the Keshan disease in China. Zn, Fe, Mo and Cu are antagonists (WHO 1996a). Mo deficiency caused irritability followed by coma, arrhythmia and night blindness. Mo supplementation removed the symptoms (Abumrad et al. 1981).

Excess Negative effects of Mo were found on reproduction and foetal development in rats and mice at a dose of 1.6 mg/kg bodyweight/day (Vyskocil and Viau 1999). One patient who had consumed a cumulative dose of 13.5 mg Mo (300–800 micrograms Mo/day) suffered from acute psychosis with visual and auditory hallucinations, a series of petit mal seizures, and one life-threatening grand mal attack. The symptoms remitted several hours after the start of chelation therapy with calcium ethylene diamine tetraacetic acid (CaEDTA). One year after the Mo poisoning, the patient was diagnosed with toxic encephalopathy with executive deficiencies, learning disability, major depression, and post-traumatic stress disorder (Momcilovic 1999).

From drinking water Studies on the influence on the human body of Mo from drinking water are rare. Concentrations of Mo in drinking water do not generally exceed 10 μg/L (Greathouse and Osbome 1980), and concentrations were even lower than 2 μg/L in studied waters in England and Wales (Smedley et al. 2014). Rosborg et al. (2003) report average concentrations of Mo in acid well waters to be 0.1 μg/L, and alkaline well waters 3.81 μg/L. Mo concentration in European bottled water was < 0.02–74 μg/L (Reimann and Birke 2010), while tap water levels of 580 μg/l have been reported in Colorado (Chappell 1979). Ranges of Mo levels were substantially higher in alkaline ground-waters, 0.3–14.8 μg/L, when compared to acidic ground-waters, 0–0.37 μg/L, and Mo was the only element among 50 that was significantly higher in alkaline well waters, women's hair, soil samples and vegetables cultivated in an alkaline area in Sweden when compared to acid. Mo concentration in well water was mirrored in hair of women. Women living in the alkaline area were healthier (Rosborg 2005). The caries-protective action of 0.1 μg/L Mo as a supplement to drinking water at pH 6.0, 7.0 and 8.0, respectively, was demonstrated in three generations of rats (Adler and Porcsalmy 1961). WHO guideline value is 0.07 mg/L (WHO 2017). EU (1998) has no established guideline value.

Suggested range Risk-reducing Mo range appears to be 0.005–0.05 mg/L.

4.2.11 Nickel (Ni), (see also 5.1.14)

In the body Ni is essential for the lower forms of life, where it reacts with other functions as a part of enzymes. The thyroid and adrenal glands in humans contain relatively high Ni concentrations (Bowman and Russell 2006). Changes induced by Ni deprivation in rats included impaired reproduction, impaired bone health, altered carbohydrate and lipid metabolism, decreased Fe status or utilization and altered thyroid hormone metabolism (Nielsen 2006a). Nutritional amounts of Ni improved bone strength in rats, and alleviation of renal damage and high blood pressure in rats (Nielsen 2006b). One study on humans show that in haemodialysis patients, serum Ni concentration was negatively correlated with plasma total homocysteine, indicating protection against, e.g., oxidation by free radicals and negative influence on the thyroid (Katho et al. 2008). Normally the daily intake is less than 150 μg (WHO 1996a).

Deficiency Ni deprivation negatively influences reproductive function, carbohydrate and fat metabolism and bone strength (Bowman and Russell 2006).

Excess Ni intake via lungs may cause cancer. Ni salts act to erode the intestines (WHO 2005). Ni-plated products in contact with skin may cause contact dermatitis (WHO 2017). Systemic contact dermatitis can develop in 1–3% nickel-sensitive individuals after oral nickel exposure, e.g. if water contains nickel 100–500 μg/L (Jensen et al. 2006), which may happen in the first flush in new sanitary tapware. Ni intake via lungs may cause cancer. Ni salts act to erode the intestines (WHO 2005).

From drinking water Normally Ni concentration in drinking water is less than 0.02 mg/L. Release of Ni from pipes and containers of acid beverages or soft drinking water and natural or industrial Ni deposits in the ground may increase Ni concentration up to 1 mg/L, thereby giving a significant contribution to the total Ni intake (Grandjean 1984). Peak values of Ni found in drinking water (0.5–1.0 mg/L) can cause systemic dermatitis in 0.1–0.2% of general population, i.e. 1–3% of people sensitive to Ni. In allergic persons, manifestations of dermatitis appear even upon oral intake of Ni. Repeated exposure to Ni, apparently even to relatively low doses, increases the probability of acquiring hypersensitivity and allergic reactions. The number of persons sensitive to Ni increases with age. Therefore, it is desirable to also minimize exposure to it through drinking water (Kozisek et al. 2010). The WHO (2017) guideline value is 0.07 mg/L and the EU (1998) parametric value is 0.02 mg/L.

Suggested upper limit Risk-reducing Ni concentration appears to be <0.05 mg/L. If proven essential: 0.01–0.05 mg/L.

4.2.12 Phosphate (PO$_4$)

Function in the body Phosphate is one of the body's electrolytes. Bone contains about 85% of the body's phosphate. The rest is located primarily inside cells, where it is involved in energy production, and muscular work energy is stored as ATP (adenosine-tri-phosphate). Phosphate is necessary for the formation of teeth, and used as a building block for several important substances, including cell membranes and DNA (deoxyribonucleic acid) (Lewis 2017). Intake of PO_4 is also important for the production of erythrocytes, and therefore influences the haemic oxygen concentration in blood. pH of the body liquids is partly regulated by the different phosphate ions (Bowman and Russell 2006). RDI is 800–1200 mg (Sonesson and Sonesson 2001; Shils et al. 1999).

Deficiency When phosphate level in blood falls dangerously low, because the body uses large amounts of phosphate during recovery from, e.g., severe undernutrition, or due to especially chronic diarrhoea or use of diuretics for a long time, muscle weakness develops, followed by stupor, coma and death. In mild chronic low phosphate, the bones can weaken, resulting in bone pain and fractures, and people become weak and lose their appetite (Lewis 2017).

Excess In people with severe kidney dysfunction causing excess phosphate, calcium combines with phosphate, which lowers calcium levels in the blood, and causes muscle cramps and spasms but also an increase in parathyroid hormone levels, resulting in bone weakness and other problems. The calcium and phosphate also form crystals (calcify) in body tissue, including within the walls of blood vessels and skin. Severe arteriosclerosis (hardening of the arteries) can result, leading to stroke, heart attack, and poor circulation (Lewis 2017).

From drinking water Studies on the influence on the human body of PO_4 from drinking water were not available. However, PO_4 in drinking water is in general very low, <10–100 µg/L, unless contaminated by fertilizers or leakage from manure pits. Ortho-phosphate has increasingly been used to decrease Pb dissolution from pipes, especially in the UK, at a dosage of approximately 3 mg/L (Hayes et al. 2008), and to decrease Cu corrosion (WHO 2017). However, this useful effect may be neutralized with negative influence on bioavailability of water calcium and magnesium – formation of an insoluble calcium-magnesium-phosphate complex decreases real intake of Ca and Mg (Monarcha et al. 2009). The daily requirement is generally assumed to be provided from one's diet. There is no guideline value for PO_4 in drinking water (WHO 2017; EU 1998).

Suggested range Risk-reducing PO_4 range is difficult to set, but a suggestion is 0.02–0.1 mg/L.

4.2.13 Rubidium (Rb)

In the body Rb is an alkali metal like Na, K and Li. Rb is not regarded essential for humans. Rb often appears along with K, and may in the event of K deficiency compensate for K. Daily intake is estimated to be 1–5 mg (Bowman and Russell 2006). The food of Hopi Indians is higher in all the essential minerals than conventional foods and also in Rb (Brewer 1984).

Deficiency Studies indicated that animals with Rb deficiency suffered from depressed food intake, milk production, growth and life expectancy (Bowman and Russell 2006). It has been shown that Rb, in contrast to Li, given to rats for 10 days facilitates the turnover of noradrenalin (Stolk et al. 1970). Thus, it has been hypothesized that Rb may have an application in the treatment of depression (Fieve and Meltzer 1974).

Excess When more than 50% of the K in the muscle tissues of rats was replaced with Rb, the rats died (Meltzer 1991). Rb levels were increased in tumorous tissues, and blood levels were lower for those with cancer than for healthy individuals (Shenberg et al. 1994; Shenberg et al. 1995).

From drinking water Rb is seldom analysed, and studies on health impact of Rb from drinking water are not available, but concentrations in South Swedish public waters were 0.1–11 µg/l (Rosborg et al. 2005). Concentrations in studied well waters in Turkey were all below 1 µg/L (Cetin et al. 2017). No guideline values are established (WHO 2017; EU 1998).

Suggested range Risk-reducing range for Rb is difficult to set with today's knowledge, but a suggestion is 0.01–0.1 mg/L.

4.2.14 Selenium (Se)

Function in the body Se is essential to humans and part of some very important antioxidants, as well as some very specific amino acids (Schomburg 2011; Triggiani et al. 2009), and is required for the proper functioning of the thyroid, testes, prostate, brain and for muscle development and function (Berr et al. 2012; Fairweather-Tait et al. 2010; Lescure et al. 2008; Lescure et al. 2009; Rayman et al. 2006; Schweizer et al. 2011). Se protects from mercury (Hg) and methyl Hg toxicity by preventing damage from free radicals or by forming inactive Se-Hg complexes (Goyer 1995). Se has been demonstrated to have anti-carcinogenic properties (Muecke et al. 2010). RDA for adults is 50 µg/day (NSFA 2012), and 55 µg/day according to NIH, National Institutes of Health (2017). Sufficient Se intake is approximately 200 µg/day, and appears to reduce the risk of some forms of cancer, especially prostate cancer (Yang et al. 1988).

Deficiency People with different diseases, ranging from rheumatoid arthritis to cancer, often have low levels of Se in their bodies (Canter et al. 2007; WHO 2017). Kaschin-Beck's disease, a disease of the bone mainly known from China, with deformities of bones and joints, is related to Se deficiency (WHO 2017). The Keshan disease, which appears predominantly in parts of China, with pericardial oppression and pain, nausea and vomiting, in some cases ending in death due to heart failure, is connected to low Se and Mo concentrations in grains and drinking water (Yang et al. 1988).

Excess Excessive Se levels decrease sperm mobility (Hawkes and Turek 2001). Ingestion of gram mass quantities cause a garlic odour in the breath, and changes in structure or loss of nails and hair, neurological disturbances, acute respiratory distress syndrome, myocardial infarction, liver cirrhosis, renal failure and death (WHO 2017; Bowman and Russell 2006; Sutter et al. 2008). In some areas around the world, Se is in excess, due to e.g., coal mining. Thus, in a region in Midwest China more than half of the population was affected by elevated Se from combustion of coal, locally cultivated vegetables and drinking water. People suffered from skin lesions, brittle and colourless hair, brittle nails, pain in extremities and peripheral anaesthesia, as well as even loss of nails and hair (Yang 1983; Zeng et al. 1999).

From drinking water Levels of Se in groundwater and surface water range from <0.1 μg/L to approximately 400 μg/L. In some areas, Se levels in groundwater may approach 6000 μg/L (WHO 2017). Swedish women drinking acid well waters had no detectable levels of Se in their hair, and there were very low concentrations in their well waters, <1 μg/L. These women also reported poorer health than women consuming alkaline well waters, who had detectable levels of Se in hair (Rosborg et al. 2002, 2003, 2005). The Keshan disease with, in the worst case, heart failure in parts of China is connected to low Se, and Mo concentrations in grain and drinking water (Yang et al. 1988). The provisional guideline value is 40 μg/L (WHO 2017) and 10 μg/L (EU 1998). However, the USA and South Africa both apply 50 μg/L (Chapman 2011) (Fig. 4.5).

Suggested range Risk-reducing Se range appears to be 0.005–0.03 mg/L.

Fig. 4.5 The Kaschin-Beck's disease, a disease of the bone mainly known from China, is related to Se deficiency (KBDF, Kashin-Beck Disease Fund 2014)

4.2.15 Silicon (Si)

Function Si is the second most abundant element in the Earth's crust, 28% (Sjöberg 1996). In 1970, Carlisle suggested that Si is a positive factor in bone calcification. Si is included in connective tissues, such as skin, nails, hair, trachea, tendons and aorta. Si is at pH levels below 9, predominantly present as $Si(OH)_4$ in water or as dimers or polymers of the $Si(OH)_4$ monomer. Since $Si(OH)_4$ is relatively inert, Si was for decades regarded as non-reactive with bio-molecules. Daily intake may vary between 20 and 1200 mg (Jugdaohsingh et al. 2002; Reffitt et al. 1999). Dietary guidance is 25–30 mg/day (Bowman and Russell 2006). Silicon controls the metabolism of Ca and Mg, and acts as an antagonist against Al (Kaizer et al. 2005; Nedzvetsky et al. 2006; Walton 2005).

Deficiency Si deficiency can cause CNS (Central Nervous System) injuries in animals, especially in the brain, and disturbed formation impacts for connective tissue and bone tissue, skin, nails and teeth (Exley 1998; Schwarz and Milne 1972). Serum markers on bone formation were positively correlated to dietary Si intake in women aged 50–62 years (Macdonald et al. 2011).

Excess Silica kidney stones were formed after taking magnesium trisilicate for several years (Haddad and Kouyoudmdidjian 1986).

From drinking water Drinking water concentrations are generally below 10 mg/L. In European bottled waters, the range was 0.3–3 mg/L (Reimann and Birke 2010). High Si concentrations in drinking water may protect against impairment of cognitive function, possibly due to Si being antagonistic against Al, and the potential role of Al in Alzheimer's disease (Kaizer et al. 2005; Nedzvetsky et al. 2006; Walton 2005) and atherosclerosis (Schwarz et al. 1977). Si concentrations in human urine increased significantly through 12 weeks of drinking bottled water with an Si concentration of 86 mg/L, indicating that Si-rich water is an effective way of providing easily absorbed dietary Si to the body (Zhaoping et al. 2010). However, Si did not affect bone turnover markers. Si concentrations were significantly lower in acid well waters compared with alkaline, average 1.7 mg/l and 2.6 mg/L, respectively (Rosborg et al. 2002). There is no guideline value (WHO 2017; EU 1998).

Suggested range Risk-reducing Si range appears to be 2–10 mg/L.

4.2.16 Vanadium (V)

Function in the body V is not proven essential (Anke et al. 1984). V is naturally present in soil, water and air, and it is also an industrial pollutant, since oil refineries and power plants use V-rich fuel oil and coal (Fallico et al. 1998; Sciacca et al. 2011). Typical intakes of V are 6–18 µg/day (Bowman and Russell 2006). Valco and Moncol (2009) suggest 10–100 µg/day as safe and adequate. Vanadium mimics insulin-like actions in humans (Marzban and McNeill 2003). V may act as a co-factor of enzymes and is involved in blood sugar metabolism, bone and tooth development, fertility, thyroid function, hormone production and neurotransmitter metabolism, and also inhibits cholesterol production (Valko and Moncol 2009).

Deficiency V deficiency studies on goats indicate skeletal deformities, miscarriage, and decreased milk production (Anke et al. 1984), and studies on humans indicate vascular diseases (Masironi 1969; Voors 1971). V deprivation resulted in swollen joints, skeletal deformations, and decreased life-span in goats (Nielsen 1998). In addition, too low levels of V altered thyroid hormone metabolism, impaired reproduction, and altered bone morphology in rats (Anke 2005).

Excess Excess V can cause decreased appetite, depressed growth, diarrhoea/gastrointestinal disturbances and kidney and liver disorders (Valko and Moncol 2009). Barceloux (1999) conclude that the toxicity of V compounds is low. Most of the toxic effects of airborne V compounds result from local irritation of the eyes and upper respiratory tract rather than systemic toxicity (Barceloux 1999). Raised levels of V have been reported in plasma in mania and depression and raised hair levels in mania (Naylor 1984).

From drinking water Studies on the influence on the human body of V from drinking water were not available. V concentrations in surface water are generally in the range 0.04–220 µg/L, and the average concentration in tap water is approximately 0.001 mg/L (Fallico et al. 1998; Sciacca et al. 2011). Average concentrations in acid well waters were 0.3 µg/L, and 0.6 µg/L in alkaline (Rosborg et al. 2002). V in European bottled waters ranged from <0.1 to 68 µg/L (Reimann and Birke 2010; Rosborg et al. 2005). There is no guideline value (WHO 2017; EU 1998). However, FAO/WHO established an upper tolerable limit for V of 0.04 mg/day (WHO 2017).

Suggested range Risk-reducing V range is difficult to set, but a suggestion is 0.001–0.01 mg/L.

4.2.17 Zinc (Zn)

Function in the body Zn is essential to humans and an important constituent of a large number of enzymes, and is obligatory for protein and DNA synthesis and cellular division, and as a stabilizer of molecular structures of sub-cellular constituents and membranes. It is very important for proper growth, wound healing and the immune system. Sufficient Zn is especially important for infants and elderly people (Bowman and Russell 2006; Martin 2011). Requirements are 2.5–4 mg/day (Bowman and Russell 2006), while WHO considers the daily recommended intake to be approximately 15–20 mg/day (WHO 2017). Zinc is known to inhibit Cu utilization (Klevay 1975; Klevay 1980; Underwood 1977), and Zn, Fe, Mo, and Cu are antagonists (WHO 1996a).

Deficiency Zn deficiency symptoms include retarded growth, depressed immune function and wound healing, skin lesions, depressed appetite, smell and taste, white spots on nails, stinging hair loss, skeletal abnormities, impaired reproductive ability, low sperm count and anorexia (Martin 2011; WHO 1996a).

Excess Intake of more than 4–8 g may give symptoms like diarrhoea, vomiting, nausea, fever and lethargy (WHO 1996a), irritability, and headache (NRC 1978).

From drinking water The concentration of Zn in natural surface waters is usually below 10 μg/L, while 10–40 μg/L in ground-waters (Friberg 1986), but can be much higher as a result of leaching of Zn from pipes and fittings (WHO 1996b). Thus, elevated Zn may originate from newer galvanized plumbing materials (WHO 2017). Zn levels in European bottled waters are reported to be in the range < 0.2–651 μg/L (Reimann and Birke 2010) and concentrations in ground-waters were in the range 1–1300 μg/L, median acid well waters 58 μg/L and alkaline 43 μg/L (Rosborg et al. 2002). In a recent study, water samples from families with a child with diabetes had lower concentration of zinc than samples from control families (Samuelsson et al. 2011). The WHO guideline value for aesthetic concerns is 3 mg/L. It is opalescent, develops a greasy film when boiled and has an undesirable astringent taste (WHO 2003, 2017). In the EU Drinking Water Directive, zinc is not mentioned (EU 1998) (Table 4.1).

Suggested range Risk-reducing Zn range appears to be 0.02–0.2 mg/L.

Table 4.1 Micro-nutrients in drinking water, in summary

Element	Rec. range	WHO limit	Role in the human body	Special comments	General origin if present in water	Health effects when from water	RDA/RDI	Contribution to daily intake, 2Liter consumption, studied Swedish waters
Boron (B)	0.1–1 mg/L	2.4 mg/L	Bones and joints, against arthritis, allergy, skin disorders, brain function and composition, immune response.	Concentrations in groundwater from <0.3 to>100 mg/L.	Bedrock, and contamination from e.g. glass production.	Beneficial effect <1 mg/L (birth rate, death rate).	Normal daily intake: 1–13 mg.	n.a.
Chloride (Cl)	20–50 mg/L	250 mg (give undesirable taste)	Most in the extracellular fluid, needed for HCl producton, in collagen and connective tissue.	Intake of Cl pursues the Na intake, >250 mg/L gives taste.	Seawater intrusion, road salt, bedrock, industrial effluents.	Corrosion, dissolution of pipe material (e.g. Cu, Pb) at >100 mg/L.	Recommended daily intake <3 g	Well water: 0.3–11% Bottled: 0.03–11%
Chromium (Cr III)	0.01–0.05 mg/L	50 μg/L (prov.)	Sugar metabolism. Low Cr is connected to heart diseases.	Oxalate decreases uptake, Fe acts antagonistic.	Bedrock	Levels in general 0.5–2 μg/L, 10–15 μg/L beneficial. Allergic dermatitis at high levels.	Normal daily intake: 50–200 μg, median 50 μg	Well water: 0–2.4% Bottled: 0–69%
Cobalt (Co)	0.005–0.02 mg/L	n.e.	Part of Vit B-12, which is synthesized by bacteria in digestive tract, stimulates production of red blood cells. Important for: spinal cord, nervous system, avoid pricking sensation and numbness of extremities.		Bedrock		Daily intake in general from some μg to 1 mg, median 8 μg. RDA: n.a.	Well water: 0–200% Bottled: 0.3–1%

(continued)

Table 4.1 (continued)

Element	Rec. range	WHO limit	Role in the human body	Special comments	General origin if present in water	Health effects when from water	RDA/RDI	Contribution to daily intake, 2Liter consumption, studied Swedish waters
Copper (Cu)	0.02–0.2 mg/L	2 mg/L (staining)	Needed for energy production, antioxidant, iron utilization, cardiovascular health. Overload may cause Wilson's disease, Menke's syndrome.	Flushing eliminates Cu. Cu in water is mirrored in hair. Zn, Fe and Mo are antagonists. Anti-microbial.	Corrosion of Cu pipes and fittings.	Levels above (0.2-) 1 mg/L may cause intestinal problems, mainly diarrhea. Infants fed inf. formula most sensible.	RDI: 0.9 mg	Well water: 0–256% Bottled: 0–1.2%
Fluoride (F)	0.5–1.0 mg/L	1.5 mg/L	Healthy teeth, protects against pathological demineralization of calcified tissues. High levels cause dental fluorosis, and skeletal fluorosis, with increased risk of fracture.		Bedrock or fluorination of drinking water.	Prevents dental caries (≈0.8–1.2 mg/L). High levels, >1.5 mg/L, may cause dental and at higher levels; skeletal fluorosis.	3–4 mg	Well water: 0–62% Bottled: 14–218%
Iodide (I)	0.005–0.05 mg/L	n.e.	Thyroid (regulation of carbohydrate/fat metabolism, reproductive function, growth and development). Deficiency causes goiter and mental retardation.		Bedrock, fortification occurs.	Goiter uncommon if >50 μg/L. High levels may cause detrimental effects on children intelligence (hundreds of μg/L).	150–300 μg	n.a.

Iron (Fe)	0.02–0.2 mg/L	0.2 (taste and appearance)	In hemoglobin/myoglobin. Excess - hemochromatosis (mainly men), Fe accumulated in liver (lethargy, abdominal pain, metabolic acidosis, liver damage). Mg (and Ca) supplementation decreases the symptoms.	Conc. > 0.2 mg/L cause rusty precipitates, coloring of washed clothes.	Bedrock, or dissolved from Fe pipes. Fe filter -Fe2+ is oxidized to Fe3+, captured in sand.	Corrosive effect on digestive tract, acute mucosal damage, diarrhea. May cause bacterial growth in pipes. Mn and Fe covary. Fe in drinking water is mirrored in hair.	15 mg	Well water: 0–46% Bottled: 0–1.3%
Lithium (Li)	0.01–0.1 mg/L	n.e.	Low intake of Li is reported to increase risk of suicide behavior, cause mental disorders (bipolarity).		Bedrock	Lower incidence of violent crimes, suicide, hypothyroidim, heart diseases in areas with high levels in drinking water.	Daily intake normally 0.2–0.6 mg. Pharmacological intake is around 140–210 mg/day.	Well water: n.a. Bottled: 0.1–119%
Manganese (Mn)	0.005–0.025 mg/L)	0.4 mg/L	Enzyme cofactor, antioxidant, important for carbohydrate, amino acid, lipid, steroid metabolism. Deficiency; osteoporosis, diabetes, epilepsy, atherosclerosis, impaired wound healing, and cataracts. Excess: hyperirritability, hallucinations, violent behaviour.	Elevated Fe and Mn causes black (Mn) and rusty (Fe) precipitates.	Bedrock.	Taste and appearance affected if >0.1 mg/L (low pH and oxygen). Alterations in Fe status, negative effects on nervous system from intake of drinking water with >600 μg/L.	Safe and adequate intake: 2–5 mg	Well water: 0.1–13% Bottled: 0–3.2%

(continued)

Table 4.1 (continued)

Element	Rec. range	WHO limit	Role in the human body	Special comments	General origin if present in water	Health effects when from water	RDA/RDI	Contribution to daily intake, 2Liter consumption, studied Swedish waters
Molybdenum (Mo)	0.005–0.05 mg/L	0.07 mg/L (n.e.)	Enzymes (conversion of sulfite to sulfate), detoxification (liver). Deficiency: disturbances in uric acid metabolism (liver), depressed food consumption/growth, infertility, elevated mortality.	Cu is antagonist (Mo decreases symptoms of Cu overload and vice versa). Mo in water is mirrored in hair.	Bedrock	Higher levels in alkaline well waters, women's hair, soils and vegetables than in acid. Women from alkaline areas reported better general health.	RDA 45 µg	Well water: 0–18% Bottled: 0–29%
Nickel (Ni)	<0.05 (0.01–0.05 mg/L)	0.07 mg/L	Ni intake via lungs may cause cancer. Ni-salts act corrosively in the intestines. Ni causes contact dermatitis.	Ni is essential for lower forms of life. Generally flushing eliminates Ni.	Bedrock, alloys in e.g. connections and fittings.	Normally concentration is <0.02 mg/L. Ni-plated taps or natural or industrial nickel deposits in the ground may increase nickel concentration up to 1 mg/L.	Normal daily intake: <150 µg	Well water: 0–127% Bottled: 0–50%
Phosphorous (PO4)	0.02–0.1 mg/L	n.e.	Normal muscular work (ATP), production of erythrocytes, part of cell membranes, pH regulation.		Bedrock	Generally very low, <10–100 µg/L, if not contaminated (fertilizers/ leakage from manure pits). Used for Pb corrosion control.	800–1200 mg	Well water: 0–14.6% Bottled: 0–144%

Rhubidium (Rb)	0.01–0.1 mg/L	n.e.	Appears along with K.	Animals with Rb deficiency suffered from depressed food intake, milk production, and growth.		South Swedish public waters were 0.1–11 µg/l.	Estimated 1–5 mg	
Selenium (Se)	0.005–0.03 mg/L	0.04 mg/L	Antioxidant, beneficial to prevent cancer, part of some amino acids, important for immune system, activation and metabolism of thyroid hormones, in sperms and testis. Too much-decreased sperm mobility. Grams of Se leads to poisoning (garlic odour on breath), changes in structure or loss of nails and hair, neurological disturbances, liver cirrhosis, renal failure, death.	Se in water is mirrored in hair. Se protects from Hg and methyl mercury toxicity.	Bedrock	Concentrations: <0.1 µg/L to 6000 µg/L. Women drinking acid well waters had no detectable levels in hair, very low levels in well waters, and reported negative health. Low Se in drinking water: Keshan disease (heart failure), Kaschin-Beck's disease (bone and joint deformaties), cancer.	RDA: 50 µg, sufficient 200 µg.	Well water: 0.2–19% Bottled: 0–5%
Silicon (Si)	2–10 mg/L	n.e.	In collagen (tendons, skin, nails, hair), essential for growth, wound healing. Deficiency: CNS injuries in animals, disturbed formation connective/bone tissues, skin, nails and teeth. Depressed levels in processed food (less fibres).	Controls the metabolism of Ca and Mg. Antagonistic against Al.	Bedrock	Drinking water concentrations generally around or below 10 mg/L. Si from drinking water may protect against impairment of cognitive function, antagonist agianst Al.	Dietary guidance: 25–30 mg.	Well water: 0.2–15% Bottled: 6–60%

(continued)

Table 4.1 (continued)

Element	Rec. range	WHO limit	Role in the human body	Special comments	General origin if present in water	Health effects when from water	RDA/RDI	Contribution to daily intake, 2Liter consumption, studied Swedish waters
Vanadium (V)	0.001–0.01 mg/L	n.e.	Deficiency give skeletal deformaties, miscarriage, decreased milk production on goats. Studies on humans indicate vascular diseases. V shows insulin-like actions in humans.		Bedrock. Industrial pollutant (oil refineries and power plants use vanadium rich fuel oil and coal).	Concentrations is generally 0.04–220 μg/L.	Typical intakes of V are 6–18 μg	Well water: 0–42% Bottled: 0–1400%
Zinc (Zn)	0.02–0.2 mg/L	3 mg/L (aes-thetic)	In a large number of enzymes; important for proper growth, wound healing, immune sytem. Severe Zn deficiency causes growth retardation, delayed sexual and skeletal maturation, skin disorders, diarrhea, loss of appetite. >4–8 g, give diarrhea, vomiting, nausea, fever and lethargy.	Zinc is known to inhibit Cu utilization.	Bedrock, pipes, fittings.	Concentrations in Swedish well waters were 1–1300 μg/L. Levels above 3–4 mg/L give taste and a greasy film on boiling.	15–20 mg	Well water: 0–15% Bottled: 0–150%

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Chapter 5
Potentially Toxic Elements in Drinking Water in Alphabetical Order

Ingegerd Rosborg, Frantisek Kozisek, and Vasant Soni

Abstract Most toxic elements in drinking water are regulated by the World Health Organization, WHO. Elevated levels of arsenic (As) are linked to skin disorders and lung cancers. Cadmium (Cd) may cause renal effects. Lead (Pb) can cause decreased IQ in children, hypertension, and damaged red blood cell production. Nitrite (NO_2) and nitrate (NO_3) forms complex with haemoglobin, methaemoglobin, which is unsuitable for transportation of oxygen in the blood. Radon (Rn) can cause lung cancer, uranium (U) especially kidney diseases, antimony (Sb) increased cholesterol levels, and barium (Ba) intestinal and cardiovascular diseases. However, elements like Ca and Mg in drinking water may decrease negative health effects of a toxic element, and should not be decreased if they are not present in excessive amounts.

5.1 A Short Introduction to Toxic Elements

Toxic elements in drinking water are regulated by the WHO (2017a) and the EU (1998). This section presents the toxic elements and ions in alphabetical order. Elements and ions are generally presented without changes (e.g. Al instead of Al^{3+}).

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5.1.1 Aluminium (Al)

In the body Al is not an essential metal. Mean daily intake of 3–14 mg have been reported (WHO 1996a), while another source suggests 1–10 mg/day. For individuals using Al-containing pharmaceuticals, antacids, Al from food sources is less than 1% of the intake. Several dietary factors, including citrate, may affect the absorption of Al. Silicon (Si) decreases the toxicity of Al (Chadwick et al. 2007). Al is accumulated in the kidneys and brain tissue. Al interacts with Ca, F, Fe, Mg, P and Sr, and is used to treat fluorosis and to reduce P absorption in uremic patients (WHO 1996a).

From drinking water Al is a clearly powerful neurotoxicant and Al from drinking water has been documented to be of concern with respect to potential neurological symptoms, such as, Alzheimer's disease and dementia (Flaten 2001; Martyn et al. 1989; Neri and Hewith 1991) and osteoporosis in ureic patients. Al levels were increased in brains of patients exposed to dialysis (Alfrey 1993). Al in drinking water for rats altered Ca homeostasis (Chadwick et al. 2007). Age-adjusted mortality rates grouped by Al in drinking water (<0.05 mg/L controls, 0.05–0.2 mg/L, and > 0.2 mg/L) showed relative risks for dementia of 1.00, 1.15 and 1.32 in men, and 1.00, 1.19, and 1.42 in women, indicating a dose-response relationship (Flaten 1990). Aluminium dissolved from surrounding soils was one important toxicity factor of the dieback of fish in the era of acidification of lakes and streams caused by "Acid Rain" in southwest Scandinavia in the 1960s–1970s (Brown et al. 1989). No health-based guideline value is established (WHO 2017a). The EU (1998) parametric value is 0.2 mg/L.

Suggested upper limit Risk-reducing Al concentration appears to be in the range of <0.1 mg/L.

5.1.2 Ammonium (NH_4)

In the body Ammonia/ammonium, NH_3/NH_4^+, are metabolites in the body, and important in acid-base regulation and biosynthesis of purines, pyrimidines and non-essential amino acids. Daily intake is in the order of 18 mg (WHO 1996b). High intake of NH_4 causes acidosis, where body tissues become acidic, including lowered blood pH (33.7 mg ammonium per kg body weight per day), disturbed glucose tolerance, and reduced tissue sensitivity to insulin (US EPA 1989). High NH_4 intake also decreases bone mass, especially Ca content (WHO 1996a).

From drinking water Studies on the influence on the human body of NH_4 from drinking water were not available. Normal concentration in groundwater is <0.2 mg/L. Up to 3 mg/L are found naturally in water rich in humic substances or Fe (Dieter and Möller 2011), however, high levels can also be an indicator of possible bacterial, sewage or animal waste pollution. Elevated NH_4 (>1.5 mg/L) may result in elevated nitrite, due to oxidation of NH_4. Since NH_4 from drinking water is not of immediate health relevance there is no guideline value (WHO 2017a). Elevated NH_4 in water may cause corrosion (WHO 2017a). The EU parametric value is 0.5 mg/L (EU 1998).

Suggested upper limit Risk-reducing NH_4 concentration appears to be <0.5 mg/L.

5.1.3 Antimony (Sb)

In the body Sb is not an essential element. It is a rare element. There are indications that Sb may cause cancer, but this has not been proven for oral intake, such as from drinking water. Suspected reproductive effects have been reported (WHO 2003b). Sb-containing drugs are used to treat especially Leishmaniasis, a disease spread by sandflies (Yang and Sun 2010). Skin irritation and toxicity to the lungs has been reported for workers under conditions of perspiration (Schwarz-Schampera 2013). Estimated daily intake: 0.2–23 µg, median 2.6 µg (WHO 1996a).

From drinking water Concentrations in drinking water are generally <1 µg/L, but may be >100 µg/L in polluted areas from acid coal mining drainage, petroleum refining and fire retardant manufacturing. Arsenic and Sb often co-exist (Gebel 1996). High levels of Sb in drinking water may cause increased cholesterol levels, but decreased glucose levels in blood (US EPA 2012a). High levels of Sb tend to reduce As-induced chromosome mutations (Gebel 1998). The WHO (2017a) guideline value is 0.02 mg/L. The EU parametric value is 5 µg/L (EU 1998).

Suggested upper limit Risk-reducing Sb concentration should to be <0.005 mg/L.

Table 5.1 Potentially toxic elements in drinking water, in summary

Element	Range	Guideline value	In human body	Special comments	Origin if present in water	Health effects when from water	Daily intake	Contribution to daily intake, 2 Liter consumption.
Aluminum (Al)	<0.1 mg/L	n.e.	Harmful, cumulative effect, dementia, neurological and skeletal toxicity.	Al interacts with Ca, F, Fe, Mg, P and Sr, used to treat fluorosis and to reduce P absorption in uremic patients.	Bedrock, e.g.affected by anthropogenous acidification.	May cause neurological and skeletal toxicity in ureic patients, after years of parenteral Al-exposure through Al-contaminated dialysate. Al in drinking water has been related to Alzheimers disease and dementia.	Mean daily intake is around 3–14 mg	Well water: 0–36% Bottled: 0.3–4%
Ammonium (NH4)	<0.5 mg/L	n.e.	Toxicological effects at exposures >200 mg/kg body weight (disturbed nervous system/carbohydrate metabolism, acidosis, renal failure).	Indicator of bacterial, sewage or animal waste pollution, or disinfection with chloramin when present in drinking water.	Degradation of proteins, present in drinking water due to leakage from manure pits, farming or sewage water treatment.	Concentration > 1.5 mg/L may cause eleveted levels of nitrite.	Normal daily intake is around 15–20 mg	0
Antimony (Sb)	<0.005 mg/L	0.02 mg/L	Not essential	As and Sb often co-exist.	Leakage from industry, dump or sludge, dissolution from pipes or other material, PET-bottles.	Generally <1 μg/L, but may be above 100 μg/L in polluted areas, as e.g. from acid coal mining drainage, petrol refining, and fire retardants. High levels may cause increased cholesterol levels, but decreased glucose levels in blood.	Estimated daily intake: 0.2–23 μg, median 2.6 μg.	

Arsenic (As)	<0.01 mg/L	0.01 mg/L	Internal organ, and lung cancers, skin disorders gastrointestinal and cardio-vascular effects, suppressed hor-mone regulation, peripheral neur-opathy, increase in foetal loss.	As and Sb often co-exist. As was used to treat syphilis.	Bedrock	More than 130 million people from Asian count-ries have been potentially exposed to arsenic conta-mintion above World Health Organization (WHO) guideline value, with concentrations from 100 to over 2000 µg/L. as in drinking water is mirrored in hair.	Estimated daily intake (non polluted DW): 30 µg	
Barium (Ba)	<1 mg/L	1.3 mg/L	High levels cause hearing loss in rats		Bedrock	Concentration in general <100 µg/L. Elevated Ba levels may lead to intestinal and cardiovascular diseases.	Median daily intake: around 300 µg.	
Beryllium (Be)	<0.005 mg/L	12 µg/L (n.e.)	Negative influence on enzymes, causes damage to most organs. It causes gene mutations. Cancer.		Bedrock	Concentrations are generally very low; <0.005–2.7 µg/L. Health problems from Be in drinking water has not been reported.	Normal daily intake: 400 ng	
Bismuth	<0.001	n.e.	Not essential. Used in compounds to treat tumours. Fatigue, confused, apathetic, forgetful, and spasms were side effects.	Bismuth is present in certain cosmetics.	Bedrock	Studies not available.	Around 400 ng/day	

(continued)

Table 5.1 (continued)

Element	Range	Guideline value	In human body	Special comments	Origin if present in water	Health effects when from water	Daily intake	Contribution to daily intake, 2 Liter consumption.
Bromate (BrO3)	<0.01 mg/L	0.01 mg/L	Potent oxidizing agent, irritating on mucous, eyes and skin, causes cough, sore throat, vomiting, diarrhea, possibly cancer.		If present in drinking water, bromide in water has been oxidized by ozonation. Also produced in concentrated hypochlorite solutions used for disinfection.	Concentrations generally <2 µg/L-16 µg/L, in ozonated water the daily intake can be 120 to 180 µg	n.e.	
Cadmium (Cd)	<0.003 mg/L	<0.003 mg/L	High intake of Cd can cause renal effects, and elevated blood pressure. Presumed carcinogen.	Sufficient Fe status reduces uptake and retention. Zn, Cu and Cd interact. Cd intake is mirrored in hair	Bedrock, fertilizers.	Cd from drinking water may cause mentioned health effects e.g. renal effects	Mean daily intake of Cd is 10–35 µg, smoking is a significant source.	Well water: 0–36% Bottled: 0.3–4%
Cyanide (CN)	<0.05 mg/L	<0.5 mg/L (short term, calculated)	Cyanide takes the place of oxygen in the respiratory process and can cause death. Acute poisoning causes rapid breathing, cramp and other neurlogical effects.		Bedrock, mining, poisonong.	Long term exposition through drinking water may negatively influence the thyroid gland, the nervous system, cause weight loss and diabetes.		
Germanium	<0.01 mg/L	n.e.	In hair of Kashin-Beck children, Se, B and Ge levels were lower than in healthy individuals. In mice, organic Ge was considered to restore impaired immunoresponse.	Ge(IV)-polyphenols can be as anti-cancer agents.				

Lead (Pb)	<0.005 mg/L	0.01 mg/L	Can severely affect especially the central nervous system, and the kidneys, cause hyper-tension, negatively influence red blood cell produc-tion, and depress bone calcification, due to antagonistic effect on Ca.	Pb from DW constitutes a great portion of the total intake nowadays, since it's not used any more as petrol additive. Pb can antagonize cop-per, and act anta-gonistic against Ca. Pb in drin-king water is mirrored in hair.	Lead pipes, brass fittings and lead-soldered seams. Acid and low mineral water is most aggressive. Pb can easily by eliminated by flushing before use. Orthophosphate dosing decreases Pb leakage.	The IQ of children can be severely negatively affected by Pb in drinking water, and cause hyperactivity and depression, negatively influence red blood cell production, bone tissue. Acute symptoms: headache, fatigue, aching joints, coordination problems, numbness, pricking sensations and loss of memory.	Normal daily intake is 20–500 µg.	Well water: 0–16% Bottled: 0–8%
Mercury (Hg)	<0.001 mg/L	0.006 mg/L	Toxicity: Inorganic mercury toxic to the kidneys, and neuropathological effects.		Bedrock, pollution (dentists, mining, chlorene production)	Naturally occurring: < 0.5 µg/L. 5.5 µg/L Izu Oshima Island (Japan), area with volcanic activity.	Normal daily intake: 2–20 µg	Well water: 0–0.4% Bottled: 0–3%
Nickel (Ni)	<0.05	70 µg/L	Ni intake via lungs may cause cancer. Ni-salts act corrosively in the intestines. Ni causes contact dermatitis.	Ni is essential for lower forms of life. Generally flushing eliminates Ni.	Bedrock, alloys in e.g. connections and fittings.	Normally concentration is <0.02 mg/L. Ni-plated taps or natural or industrial nickel deposits in the ground may increase nickel concentration up to 1 mg/L.	Normal daily intake: <150 µg	Well water: 0–127% Bottled: 0–50%

(continued)

Table 5.1 (continued)

Element	Range	Guideline value	In human body	Special comments	Origin if present in water	Health effects when from water	Daily intake	Contribution to daily intake, 2 Liter consumption.
Nitrate (NO3)	<50 mg/L	50 mg/L	Formed when ammonium is oxidized. Excess cause methaemoglobin-aemia in infants, “blue baby”, as oxygen carrying capacity of hemoglobin is depressed.		Leakage from runoff of manure pits and inor-ganic fertilizers. In urban areas lacking centra-lized sanitation systems mostly from human waste.	Leakage from runoff of manure pits and inorganic fertilizers can increase NO3 levels in ground water to levels well above the guideline value, 50 mg/L. Excess NO3 in DW cause diarrhea, but also “blue baby” syndrome. Bottle-fed infants are at greates risk.	Normal daily intake is around 20 mg	
Nitrite (NO2)	<0.5 mg/L	3 mg/L	Excess cause methaemoglobinaemia in infants, “blue baby”, oxygen carrying capacity of hemoglobin is depressed.	Anaerobic conditions in water distribution systems may result in the formation of NO_2. Chloramination of drinking water may give rise to the formation of nitrite.	Leakage from runoff of manure pits and inorganic fertilizers, under anaerobic conditions..	Excess NO2 in DW cause diarrhea, but also methaemoglobinaemia in infants, “blue baby” syndrome. Bottle-fed infants are at greates risk.		

Radioactivity (Radon, Radium, Thorium and Uranium)	<0,1 mS/year	Total: 10 Bq/L, 0.1 mSv/year	Cell plasma, cell membranes and DNA can be damaged. Risk of cancer.	Ra, Rn, Th, and U are the predominant radionuclides in water, and may build up in treat-ment filters. Can be eliminated by aeration or boiling.	Bedrock, and accidentally from nuclear power plants.	Rn from drinking water may cause lung cancer and is, after smoking cigarettes, the most common cause of lung cancer. Rn also causes stomach cancer. U is harmful for the kidneys, and may disturb the reproductive organs.	Natural background radiation is about 1 mSv/year, indoor environment 2 mSv/year.	
Silver (Ag)	<0.01	n.e.	Bactericidal properties. Silver overload causes argyria (skin and hair are heavily discolored). Estimated oral NOAEL is 10 mg.	Some types of tap filter cans give high Ag concentrations in water, up to 50 µg/L.	Ag is seldom present in drinking-water at concentrations >5 µg/l. However, silver salts are used to maintain the bacteriological quality of drinking-water.	Ag concentration 0.1 mg/L gives a total dose over 70 years of half the human NOAEL of 10 g. Drinking-water treated with silver for disinfection, e.g. in tap filters cans, may be above 50 µg/l.	Estimated daily intake is about 7 µg.	
Strontium (Sr)	<0.2 mg/L	n.e.	Internal exposure to Sr-90, a radioactive isotope, is linked to bone cancer, cancer of the soft tissue near the bone, and leukemia.		Bedrock.	Close relationship between absorption of Ca and Sr, tends to deposit in bone and blood-forming tissue. Sr in drinking water is mirrored in hair.	Average intake around 2 mg/day.	
Tin (Sn)	<0.1 mg/L	n.e.	Irritating on gastric tract; causes vomiting. Organic Sn compounds may cause cramps and hallucinations.	Concentrations above 1–2 µg/L are rare, but 295 µg/L in one bottled water. Sn can decrease Cu, Zn, and Mn status.	Leakage from alloys, cans.		Mean daily intake is estimated to be some mg.	

(continued)

Table 5.1 (continued)

Element	Range	Guideline value	In human body	Special comments	Origin if present in water	Health effects when from water	Daily intake	Contribution to daily intake, 2 Liter consumption.
THMs (Trihalomethanes)	<0.015 mg/L	differs for the different THMs (see further above: 5.1.22)	Suspected to cause cancer, discussed in relation to reproductivity, and congenital anomalies		From chlorination or bromination of drinking water to avoid beacterial growth	A moderate association with bladder cancer	no data	
Titanium (Ti)	not set	n.e.	In dental materials and implants. Ti may be mirrored in hair, and accumulate in the lungs and lymphatic tissue.	Ti concentrations in acid well waters was <50 µg/l, up to 210 µg/L in alkaline.	Bedrock.	Titanium in water is generally correlated to Ca.	Estimated daily intake is about 0.8 mg.	
Uranium (U)	<0.010 mg/L	30 µg/L	U accumulates in the kidneys and skeleton. Negatively influences the kidneys, fertility, and the nervous system, cause oxidative stress, disturbs bone formation.	Especially α-radiation, U-238 (most abundant isoptope); halflife 0.25 billion years .U concentrations: 100–300 µg/L, common in Swedish ground waters. Euro-pean bottled waters: <0.001–229 µg/L.	Bedrock, mining.	Kidney disturbances. U in drinking water is mirrored in hair. No safe lower limit is found in drinking water. Remai-nings from U mining cause drinking water sources with elevated levels of radiation. Potential health effects include bone cancer and impaired kidney function from exposure to radionuclides in drinking water		

5.1.4 Arsenic (As)

In the body Arsenic was not confirmed as essential, but was used in medications, especially to treat syphilis, before the advent of antibiotics. Inorganic As is carcinogenic. Daily intake is <200 µg/day, generally <100 µg/day. If stated to be essential, <20 µg/day would be sufficient (WHO 1996a). Acute poisoning leads to vomiting, diarrhoea, and finally circulatory failure. The essentiality is probably connected to protein synthesis. Inorganic As(III) is more poisonous than organic As(III), which in turn is more toxic than As(V) compounds. Medication containing As is still used against sleeping sickness (Selinus et al. 2013).

From drinking water Exposure to As through drinking water is a growing public health concern. More than 130 million people from Asian countries, as well as people in parts of Argentina, Mexico, Mongolia, Thailand and Taiwan, have been exposed to As contamination, at concentrations of 100 to over 2000 µg/L (WHO 2017a; Bhattacharya et al. 2006). Ingestion of high levels of As is linked to skin (Fig. 5.1), internal organs and lung cancers; skin disorders (hyperpigmentation and keratosis); gastrointestinal effects; cardio-vascular effects; suppressed hormone regulation; peripheral neuropathy; increase in foetal loss; shortness of breath; and other respiratory effects. Malnourished people and infants are especially at risk (Bhattacharya et al. 2006). A significant increased risk of prostate cancer was seen in a dose-response manner as As concentration in drinking water increased even at low levels. The risk for aggressive prostate cancer increased with 11% in the group with median (2.07–2.98 µg/L) As concentration, and with 32% in the group with high concentration (2.99–18.6 µg/L) (Roh et al. 2017). Environmental arsenic mainly exists as sulphide complexes such as realgar (As_2S_2), or orpiment (As_2S_3) and iron pyrites (FeAsS) (Gorby 1988). High Fe concentrations in As-poisoned water, in pyrites, may be an additional cause for severe symptoms of As poisoning. If Mn is present at high concentration along with Fe and As (Fe and Mn often co-exist), the situation may be even worse (see further Fe and Mn in Chap. 4). Nano filtration, reverse osmosis (RO) or adsorption is used for treatment. If RO is used to eliminate As from water, it will decrease arsenate ions by 98% or more but it will also remove dissolved solids, thereby eliminating nutrient elements like Ca and Mg (Harisha et al. 2010). The EU (1998) parametric value and the WHO (2017a) provisional guideline value of As is 0.01 mg/L.

Suggested upper limit Risk-reducing As concentration should be as low as possible, but definitely <0.01 mg/L.

Fig. 5.1 Health effects of arsenic in an endemic area in the Huhhot PR, China (Photo: Bhattacharya P 2003)

5.1.5 Barium (Ba)

In the body Ba is not proven essential. Median daily intake is around 300 µg (Bowman and Russell 2006). There are indications that high Ba intake may lead to cardiovascular problems (Perry et al. 1989), e.g. increased blood pressure (US EPA 2013c). Exposure to high-dose Ba (>100 mg/kg/day) has been shown to cause physiological impairments (Ohgamia et al. 2012).

From drinking water Ba in drinking water in general originates from bedrock, and concentrations are mostly <100 µg/L, but levels of several mg/L have been reported, up to 15 mg/L (Flaten 1991). There is a weak connection between intestinal and cardiovascular diseases and elevated Ba levels in drinking water (Schroeder and Kramer 1974; Elwood et al. 1974; Ohgamia et al. 2012). Low-dose Ba administered by drinking water causes hearing loss in mice (Ohgamia et al. 2012). Ba administered in drinking water at levels equivalent to and ten-fold higher than the WHO guideline level caused severe hearing loss in rat (ATSDR 2005; Ohgamia et al. 2012). The EU (1998) has no guideline value. The WHO (2017a) guideline value is 1.3 mg/L.

Suggested upper limit Risk-reducing Ba concentration appears to be <1 mg/L.

5.1.6 Beryllium (Be)

In the body Beryllium is not essential, and is one of the most toxic chemicals. It has a negative influence on enzymes and causes damage to most organs in the human body. It interferes with DNA, causing gene mutations. The element can cause cancer, especially lung cancer, after occupational exposition through the lungs (NAP 2013). Normal daily intake is around 400 ng/day (WHO 2013).

From drinking water Drinking water concentrations are generally very low; <0.005–2.7 μg/L (WHO 2017a; Hasan and Kazemi 1974). Some people who drink water containing beryllium well in excess of the maximum contaminant level (MCL) for many years could develop intestinal lesions (US EPA 2013d). No guideline value is established, but 12 μg/L is mentioned (WHO 2017a).

Suggested upper limit Risk-reducing Be concentration appears to be <0.005 mg/L.

5.1.7 Bismuth (Bi)

In the body Bismuth is not essential to humans. The element is used in compounds to treat tumours, especially BIPP (Bismuth iodoform paraffin paste). One patient treated with Bi was fatigued, confused, apathetic, forgetful, and experienced spasms in his thigh muscles after such treatment (Atwal and Cousin 2016). Bismuth (often bismuth oxychloride) is present in certain cosmetics (Personal Care 2017).

From drinking water Concentration levels and studies on the influence on the human body of Bi from drinking water were not available. Bismuth thiol (BT) biocides was proposed to be used as a disinfection agent in drinking water treatment (Codony et al. 2003). No guideline values for Bi are established (WHO 2017a; EU 1998).

Suggested upper limit Risk-reducing Bi concentration is difficult to set, but a suggestion is <0.001 mg/L.

5.1.8 Bromate (BrO_3)

In the body BrO_3 is not essential. It is a potent oxidizing agent, and as such irritating on different mucous organs and skin, and kidneys are a key target (WHO 2005a). It is probably a carcinogen to humans (WHO 2017a).

From drinking water Concentrations are generally <2–16 µg/L (WHO 2017a). BrO_3 in drinking water is a by-product of bromine oxidation with ozone, and concentrated hypochlorite solutions used to disinfect, range from 120 to 180 µg/day (McGuire et al. 1990). At levels thousands of times the amount that would come from drinking water, at its standard concentration, causes cough, sore throat, vomiting, diarrhoea and possibly cancer (NYSDH 2013). BrO_3 will react aggressively with THM precursors to form THM (trihalomethanes), which are suspected but not proven to cause cancer, and are also discussed in relation to reverse reproductive outcomes and congenital anomalies in human studies (Lau 2015). Freeman et al. (2017) found a moderate association between bladder cancer and average daily intake and cumulative intake of THMs in the highest 5% (>45.73 µg/L) of exposure compared with the lowest quartile (<6.83 µg/L). Researchers collected recent annual mean THM levels in municipal DW from routine monitoring records in the 28 EU countries through a standardized questionnaire and calculated the population-weighted EU mean. A no-effect threshold for bladder cancer was observed for THMs at 15.5 µg/L. They concluded that although efforts have been made in the last years to reduce THM levels in some countries, current levels still lead to a burden of disease that could be avoided without compromising the microbiological quality (Evlampidou et al. 2019). The WHO (2017a) and EU (1998) provisional guideline value is 0.01 mg/L.

Suggested upper limit Risk-reducing BrO_3 concentration appears to be <0.01 mg/L.

5.1.9 Cadmium (Cd)

In the body Cd is not essential. Cd co-exists with Zn in the Earth's crust (Warfvinge 1998). Human exposure to Cd mostly occurs from consumption of contaminated food, tobacco smoke and inhalation by workers in the non-ferrous metal industry (WHO 2017b). Sufficient Fe status in the body reduces uptake and retention of Cd (Bunker et al. 1984) and Cd can induce hypercholesterolemia which can be relieved with extra Cu (Bordas and Gabor 1982). Cd accumulates in the kidneys, and high intake of Cd can cause renal effects (Eklund and Oskarsson 1999), and elevated blood pressure. Cd intake is measurable in the hair of persons who drink water with Cd (Medeiros and Pellum 1984). Cd also exerts toxic effects on the skeletal and respiratory systems. Cd is classified as a human carcinogen (WHO 2017b). It binds to an enzyme, metallothionine, which normally contains Zn or Cu (WHO 1996a). Daily intake is in general 10–35 µg, and smoking is a significant source (WHO 2017b).

From drinking water When Cd is present in drinking water the origin may be fertilizers, corrosion of galvanized pipes, old solders and fittings. Cd from drinking water may cause the above-mentioned health effects such as, renal effects (Eklund and Oskarsson 1999). The WHO (2017a) guideline value is 0.003 mg/L, the EU (1998) parametric value is 0.005 mg/L.

Suggested upper limit Risk-reducing Cd concentration appears to be <0.003 mg/L.

5.1.10 Cyanide (CN)

In the body CN forms a stable complex with a form of cytochrome oxidase, an enzyme that promotes the transfer of electrons in the mitochondria of cells during the synthesis of ATP in the respiratory process, and can cause death. The LD_{50} for ingestion is 50–200 mg, calculated as hydrogen cyanide (cyanidecode.org 2017). Acute poisoning occurs a few minutes after oral intake. Symptoms include anxiety, rapid breathing, nausea and vomiting, headache, cramp and other neurological effects, and coma (Hamel 2011). CN may cause vitamin B_{12} deficiency in humans, and chronic effects on the thyroid, hypothyroidism and goitre, and on the nervous system (WHO 2005b).

From drinking water CN is occasionally found in drinking water, primarily as a consequence of industrial contamination (WHO 2005b). Long-term exposure through drinking water may negatively influence the thyroid gland and the nervous system and can cause weight loss and diabetes. The WHO has not established a guideline value, with the comment “occurs in drinking water below those of health concern”, but presents a possible (calculated) short-term health-based guide value of 0.5 mg/L (WHO 2017a). The EU (1998) parametric value is 0.05 mg/L.

Suggested upper limit Risk-reducing CN concentration appears to be <0.05 mg/L.

5.1.11 Germanium (Ge)

In the body In hair of Kashin-Beck children, Se, B and Ge levels were lower than in healthy individuals (Peng et al. 2000). Ge(IV)-polyphenols can act as anti-cancer agents (Pi et al. 2013). In a study on mice, organic Ge was considered to restore to some extent impaired immunoresponse (Mitzushima et al. 1980).

From drinking water Scientific studies on Ge in drinking water were not available. EU (1998) and WHO (2017a) have not established a guideline value.

Suggested upper limit Risk-reducing Ge concentration is suggested to be <0.01 mg/L.

5.1.12 Lead (Pb)

In the body Pb is a cumulative poison that can severely affect the central nervous system, cause hypertension, negatively impact red blood cell production, disturbed function of the kidneys and depress bone calcification. Antagonism against Ca is involved. Ingested Pb is absorbed 4–5 times easier in children than in adults, and can cause decreased IQ, hyperactivity and depression (Alexander et al. 1973; Rabinowitz et al. 1973; Kordas et al. 2006; Miranda et al. 2007). Pb may increase urinary losses of Cu (Klauder and Petering 1977). Average daily intake is around 20–25 µg (Al Othman 2010).

From drinking water The use of Pb-containing additives in petrol has decreased by over 99% since 1995 and continues to decrease on a global basis, and Pb concentrations in air continues to decline. Thus, Pb intake from drinking water constitutes a greater proportion of the total intake (SCHER 2011). As late as 1965, Pb pipes were installed in some countries between the mains and the house taps. Low-mineralized water is not stabilized and is therefore highly aggressive to piping materials that it is in contact with. Other water parameters also influence Pb leaching from pipes (Anonymous 1994). Low mineralized water is, e.g., RO (reverse osmosis) water. Pb in drinking tap water can generally be reduced by flushing prior to usage. Around 25% of domestic dwellings in the EU, except in the Nordic countries, have Pb pipes (over eight million dwellings), potentially putting 120 million people at risk from Pb in drinking water (Hayes and Skubala 2009). Orthophosphate dosing, dosed at up to 3 mg/L (P), decreases corrosion of Pb pipes (Hayes et al. 2008). Foetal death rates during the Washington DC “lead crisis” in 2000–2004, when drinking water Pb levels were highest, were significantly higher compared to Baltimore; where levels were lower (Edwards 2014). Even low levels of Pb from drinking water can cause learning disabilities, shorter stature, impaired hearing, and impaired formation and function of blood cells in children. Pregnant women consuming Pb from their drinking water are at risk of reduced growth of the foetus or premature birth (US EPA 2017).The EU (1998) and WHO (2017a) guideline value is 0.01 mg/L.

Suggested upper limit Suggested risk-reducing Pb concentration is <0.005 mg/L.

5.1.13 Mercury (Hg)

In the body Hg is not an essential element. The average daily intake of Hg is in the range 2–20 µg/day (WHO 1996a). Organic Hg compounds are more readily absorbed. Methyl mercury poisonings from contaminated food may cause neurological disorders and developmental difficulties for children exposed *in utero* (Bensefa-Colasa et al. 2011). High exposures to inorganic Hg may result in skin rashes and dermatitis, mood swings, insanity, memory loss, mental disturbances, muscle weakness, damage to the gastrointestinal tract and the kidneys (Chang and Hartmann 1972; US EPA 2013a).

From drinking water Naturally occurring Hg concentrations in groundwater and surface water are <0.5 μg/L (Aastrup et al. 1995). Thus, Hg in drinking water is considered to be a minor source of exposure. However, 5.5 μg/L of inorganic Hg was reported for wells in Izu Oshima Island (Japan), where volcanic activity is frequent (Magara et al. 1989). The WHO (2017a) guideline value is 0.006 mg/L, and the EU (1998) parametric value is 0.001 mg/L.

Suggested upper limit Risk-reducing Hg concentration appears to be <0.001 mg/L.

5.1.14 Nickel (Ni), see further 4.2.12

5.1.15 Nitrate (NO_3)

In the environment NO_3 is part of the nitrogen cycle, and NO_3 is formed when NH_4 formed from urea in faeces and urine is oxidized (Bowman and Russell 2006).

From drinking water NO_3 levels are normally less than a few mg/L. However, NO_3 is readily soluble in water, and leakage from runoff of manure pits and inorganic fertilizers in agricultural land can increase levels in groundwater to well above the guideline value, 50 mg/L. In urban areas lacking centralized water and sanitation systems, nitrogen from human waste appears to be the most important source. Bottle-fed infants may be at risk if NO_3 concentrations are high in water, since NO_3 may be reduced to nitrite, NO_2, in the stomach of very young infants, and nitrite may complex haemoglobin (Hb) to form methaemoglobin (metHb), which cannot transport oxygen around the body, and which may cause "blue-baby" syndrome (WHO 2003c). Many studies also show that elevated NO_3 levels in drinking water cause diarrhoea, and Gupta et al. (2001) reported that elevated NO_3 levels may cause cancer (Bogovski and Bogovski 1981), but these results are questioned. The role of NO_3 exposure alone in causing methaemoglobinaemia has been questioned (Avery 1999; Fewtrell 2004). The guideline value is 50 mg/L (WHO 2017a; EU 1998).

Suggested upper limit NO_3 concentration should be <50 mg/L.

5.1.16 Nitrite (NO_2)

In food NO_2 is used as a food preservative, especially in cured meats (Bowman and Russell 2006).

From drinking water Nitrification combined with anaerobic conditions, as a consequence of microbial activity in distribution systems, can increase nitrite levels in general to 0.2–1.5 mg/L. NO_2 is 10 times more potent than NO_3 on a molar basis with respect to methaemoglobin formation −see nitrate above. Chloramination of drinking water may give rise to the formation of nitrite, although nitrate is the more common end product. At extreme NO_2 concentrations, asphyxia can occur (WHO 2003c).The WHO (2017a) guideline value is 3 mg/L, to protect against methaemoglobinaemia in bottle-fed infants due to short-term exposure, and EU (1998) parametric value is 0.5 mg/L.

Suggested upper limit NO_2 concentration should be <0.5 mg/L.

5.1.17 Radioactivity

In the body Naturally occurring radioactive elements are present in certain rocks. “Natural background radiation” outdoor is approximately 0.3–1 mSv/year, and indoor environment 0.2–1 mSv/year (WHO 2017a). Acute signs of exposure to extreme levels of radioactivity are feeling of sickness, vomiting, diarrhoea, bleeding, coma, and in the worst case death. However, long-term exposure to naturally occurring radioactive elements leads to chronic health effects, like development of different forms of cancer (ICRP 2017).

From drinking water The predominant radioactive elements in drinking water include radon (Rn), uranium (U), radium (Ra), and thorium (Th) (see also Table 5.2). Drinking 730 L of drinking water with Rn-222 of 500 Bq/l would contribute by a yearly dose of 0.1 mSv. Rn is a gas and can easily be degassed from drinking water during different household uses. Inhalation of radon from drinking water may cause lung cancer and is, after cigarette smoking, the most common cause of lung cancer in some countries. Standard water treatment procedures at water works may remove radioactive elements. Controlled dilution of contaminated water with non-contaminated water is another option. Radio nuclides may build up in treatment filters, tanks and pipes at treatment plants (Gafvert et al. 2002). During the era of spas, people went to certain wells to drink water containing radioactive nuclides

Table 5.2 Main Radioactive components in drinking water and its guidelines values

Guideline value (Bq/L)			
0.1	1	10	100
Pb-210	U-234	U-238	C-14
Po-210	Th-228	Cs-134	
Ra-228	Th-230	Cs-137	
	Th-232	Sr-90	
	Pt-239	I-131	
	Am-241		

(Bergmark 1959), but it was only short-term exposure, maximum weeks or month. Indicative dose is 0.1 mSv/year (WHO 2017a; EU 1998).

Suggested upper limit Suggested level is < 0.1 mSv/year.

5.1.18 Silver (Ag)

In the body Ag is increasingly being recognized for its bactericidal properties and used in treatments against Legionnaires disease. Phoenicians used Ag vessels to keep water, wine and vinegar pure during their long voyages. In America, pioneers moving west put Ag and Cu coins in their water barrels to keep them clean (Doulton 2012). Estimated daily intake is approximately 7 µg. A sign of Ag overload is argyria; a condition in which skin and hair are heavily blackened. Estimated oral NOAEL (No Observed Adverse Effect Level) for argyria in humans for a total lifetime intake is 10 g of Ag (WHO 2017a). However, recent review suggests that silver particles may be genotoxic for mammals and humans (Fewtrell et al. 2017).

From drinking water Ag is seldom present in groundwater and surface water at concentrations above 5 µg/l. Ag concentrations 0.1 mg/L results in a total dose over 70 years of half the human NOAEL of 10 g. Levels in drinking water treated with Ag for disinfection, such as in tap filters cans, may be above 50 µg/l (WHO 2017a; Rosborg 2006). There are no adequate data with which to derive a health-based guideline value for Ag in drinking water (WHO 2017a; EU 1998).

Suggested upper limit Risk-reducing Ag range is hard to set on today's knowledge, but a suggestion is <0.01 mg/L.

5.1.19 Strontium (Sr)

In the body Sr is not regarded essential. Sr usually occurs together with Ca in bedrocks, and there is a close relationship between absorption and deposition in the body of Ca and Sr (Hutchison et al. 1992). Sr in strontium ranelate, an organic compound including Sr, is used to increase bone formation (Meunier et al. 2004; Marie et al. 2001). The average daily intake of Sr in Finland was 1.9 mg, while it was 2.3 mg in Japan (Varo et al. 1982; Shiraishi et al. 1994). Sr has radioactive isotopes.

From drinking water Sr in drinking water is mirrored in the hair of those who drink such water (Hopkins et al. 1963; Rosborg et al. 2002). Internal exposure to Sr-90, the radioactive isotope of Sr, is linked to bone cancer, cancer of the soft tissue near the bone and leukaemia (US EPA 2012b) (cf. Radioactivity above). Elevated Sr concentrations can be associated with Fe-corrosion products (Gerke et al. 2013). There is no established drinking water guide line value for non-radioactive Sr-88 (WHO 2017a; EU 1998). US EPA reporting threshold is 0.3 mg/L (Gerke et al. 2013).

Suggested upper limit Risk-reducing upper limit for Sr-88 is suggested to be <0.2 mg/L.

5.1.20 Tin (Sn)

In the body Sn is not stated as essential to humans. Sn concentrations in foodstuff stored in un-lacquered cans frequently exceed 100 μg/g, but are now below 25 μg/g due to the use of lacquered coated cans. Organic Sn compounds are used as biocides and antifouling agents. Mean daily intake is estimated to be 1–40 mg (WHO 2004). Amounts of Sn similar to those found in human diets can depress Zn, Mn and Cu status. Sn is irritating on the gastric tract and causes vomiting. On the other hand, dietary deficiency of Sn has been reported to cause depressed growth and response to sound (Bowman and Russell 2006; Pekelharing et al. 1994).

From drinking water Sn concentrations in drinking water above 1–2 μg/L are rare (WHO 2004), which explains why drinking water is not a significant source of tin for the general population. However, a concentration 295 μg/L has been found in bottled mineral water (Allen et al. 1989). Organic Sn, DiMethyl Tin (DMT), in drinking water caused developmental neurotoxicity in offspring of rats (Ehman et al. 2007). There is no established drinking water guide line value (WHO 2017a; EU 1998).

Suggested upper limit Risk-reducing upper limit for Sn appears to be <0.1 mg/L.

5.1.21 Titanium (Ti)

In the body Ti is not stated essential. Ti is a component of various types of rock. Ti may accumulate in the lungs and lymphatic tissue. Estimated daily intake is approximately 0.8 mg. The metal is used in dental material, filler in medicines, hip, and knee implants (Lenntech 2013).

From drinking water Ti concentrations in water are very low, usually <1 μg/l. Average Ti concentrations in acid well waters in southern Sweden were 1.7 μg/L and average alkaline 1.5 μg/L (Rosborg et al. 2002). There is no established guideline value (WHO 2017a).

Suggested upper limit Risk-reducing upper Ti limit is not possible to set based on today’s knowledge.

5.1.22 Trihalomethanes (THMs)

In the body (Trihalomethanes) are suspected but not proven to cause bladder cancer, and are also discussed in relation to reverse reproductive outcomes and congenital anomalies in human studies (Lau 2015)

From drinking water Freeman et al. (2017) found a moderate association between bladder cancer and average daily intake and cumulative intake of THMs in the highest 5% (>45.73 µg/L) of exposure compared to the lowest quartile (<6.83 µg/L). Researchers collected recent annual mean THM levels in municipal DW from routine monitoring records in the 28 EU countries through a standardized questionnaire and calculated the population-weighted EU mean. The estimated weighted-mean THM level was 11.7 µg/L and country average estimate was above this level in ten countries. Maximum levels exceeded the EU regulatory limit (100 µg/L) in nine countries. The authors concluded that about 5% (i. e. about 6500 cases) of bladder cancers in the EU may be attributable annually to THMs exposure though drinking water. They concluded that although efforts have been made in the last years to reduce THM levels in some countries, current **levels still lead to a burden of disease that could be avoided without compromising** the microbiological quality (Evlampidou et al. 2019). The WHO (2017a) guideline values are: chloroform 0.3 mg/L, bromoform 0.1 mg/L, dibromochloromethane 0.1 mg/L, bromdichloromethane 0.06 mg/L. The EU (1998) parametric value is 0.1 mg/L.

Suggested upper limit THMs should be kept as low as possible (preferably <0.010 mg/L), but without compromising microbial safety.

5.1.23 Uranium (U)

In the body Uranium is not essential. U accumulates in the kidneys and skeleton, but little is found in the liver (La Touche et al. 1987). The average normal half-life of U in humans has been estimated to be 180–360 days. Clearance from the skeleton is slowest (Berlin and Rudell 1986). The U heavy metal properties are discussed more as health threatening than the fact that U is radioactive, since the half-life is very long, and therefore the radiation value is very low. U-238, which is the most abundant isotope, has a half-life of 0.25 billion years (Kurttio et al. 2002). High U intake may disturb bone formation (Milgram et al. 2007), negatively influence the nervous system (Bussy et al. 2006; Lestaevel et al. 2005) and cause oxidative stress (Taulan et al. 2004).

From drinking water Uranium concentrations in the range 100–300 µg/L were common in studied groundwaters in central and northern parts of Sweden (Ek et al. 2008), and European bottled waters had U concentrations in the range < 0.001–229 µg/L (Reimann and Birke 2010; Rosborg et al. 2005). U in drinking water results in measurable concentrations in the hair of those who drink water containing U (Karpas et al. 2005; Moss et al. 1983). U from drinking water as a cause of kidney disease has lately become an issue for drinking water producers, as no lowest limit to avoid negative influence on kidneys was found (Kurttio et al. 2002). U in drinking water can also negatively influence fertility (Raymond-Whish et al. 2007). In a German study in Bavaria, weak but significant positive associations were found between drinking water concentrations of U and malignant, benign and other growths/tumours and disease of the liver; U concentrations >10 μg/L. In addition, elevated rates of thyroid diseases seemed to occur when mean U concentrations exceeded 2 μg/L (Banning and Benfer 2017). Tailings from U mining result in drinking water sources with elevated levels of radiation. Potential health effects include bone cancer and impaired kidney function from exposure to radio nuclides in drinking water (US EPA 2013b).The WHO provisional guideline value is 0.03 mg/L (WHO 2017a). EU (1998) has not established a guideline value.

Suggested upper limit Risk-reducing U upper limit is suggested to be <0.010 mg/L.

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Chapter 6
Technical and Mineral Level Effects of Water Treatment, Corrosion Control

Asher Brenner, Kenneth M. Persson, Larry Russell, and Ingegerd Rosborg

Abstract Hard water with salts of Ca and Mg may cause scaling, and is often softened. Water with toxic substances, e.g. heavy metals, is harmful, and is often treated with different filtering methods, nowadays often reverse osmosis (RO). There are more than 21,000 desalination plants around the world, providing more than 350 million people with drinking water, and there are more to come. RO-treated waters without pH-adjustment tend to be corrosive; causing elevated levels of metals released from especially pipes, e.g. Pb, Fe and Cu, but also lack minerals, causing decreased daily intake and loss of minerals from the body. Even pH-adjusted RO water has very low mineral content. Food boiled in such water also tends to lose minerals. There are indexes to be used as guides to choose a re-mineralization method after RO. However, methods used today don't take mineral levels in treated drinking water preferable for human consumption into account, as corrosion aspects are only considered. Treatment with dissolution of dolomitic-calcitic limestone (free from toxic elements) giving 30–80 mg/L Ca, 100–300 mg/L HCO_3, 10–50 mg/L Mg and 25–100 mg/L SO_4, with Ca/Mg 2–3:1 would be preferable for drinking water production.

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6.1 Chemical Conditions in Non-corrosive Water, and How to Produce It

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6.1.1 Introduction to Non-corrosive Water

Due to the methods used for desalination, only small amounts of organic and inorganic material can follow evaporated or permeated water. The quality of the produced desalinated water is therefore characterized by very low salinity, low pH, high aggressivity and high corrosivity. Permeate had a very low content of HCO_3^- (‹4 mg HCO_3^-/L) and Ca^{2+} (‹2.5 mg Ca^{2+} /L) and Mg^{2+} (‹4 mg Mg^{2+}/L). This corresponds to findings from many different plants in the world (e.g. USA, Australia, Middle East, North Africa).

High-purity water tends to be reactive and can cause severe corrosion on construction parts and pipes of iron, copper and concrete. Cement mortar lining of water pipes deteriorates due to corrosive attacks of soft waters at low pH. Untreated desalinated water when in contact with these materials is therefore unsuitable for direct human consumption. Re-mineralization and pH adjustment should be done especially with respect to the buffering capacity content of total hardness (TH) components (Ca^{2+} and Mg^{2+}) and to corrosion-related parameters (TDS and pH). In countries where drinking water is often produced from low-mineral rain-like surface waters, such as Finland, Norway, Sweden, Switzerland, Canada, such re-mineralization of drinking water has been done for decades. Methods used there can be applied also to desalinated water. When used for irrigation, other minerals may have to be added to the desalinated water to meet the requirements of soils and plants.

Re-mineralization may consist of different unit operations but the main processes are:

- Limestone dissolution by carbon dioxide
- Application of sodium hydrogen carbonate and calcium sulphate
- Application of hydrated lime and sodium carbonate
- Application of online micronized lime
- Application of carbon dioxide and excess hydrated lime

The objective of re-mineralization is to obtain stable non-corrosive water with minimum addition of material. Optimum levels of re-mineralization should utilize a minimum of externally added CO_2 since the acid property of carbon dioxide demands more alkalinity to be added in order to produce final product water that is non-corrosive. When designing and operating re-mineralization plants, the quality of the feed water must be known and preferably monitored through conductivity meter and pH-meter. A target water quality should be identified corresponding to the technical needs for the distribution system and, as discussed in this book, also health requirements in the future. Saturation-pH calculations can be performed or practical engineering indexes such as the Langelier Saturation Index (LSI) should be used and be close to 0. Method development such as mathematical simulations and calculation programs are available and can be downloaded from many sites. Some examples are provided below.

The composition of desalinated water differs depending on the type of plants, operating process, type of raw water and the condition of membranes. The main findings of the characteristic of desalinated waters are:

1. The contents of $Ca^{2+}$and Mg^{2+} are proportional with equation: $Mg^{2+}/L \approx 1.7 * Ca^{2+}/L$
2. The TDS/EC_{25} equitant has a value around 0.47.
3. The ratio between CL^- and Na^+ is 1.25 mmol Cl^- per mmol Na^+.
4. The turbidity with the desalinated water is around 0.2NTU, with higher values considered to be an indicator of problems in the installations, such as corrosion.
5. The pH at the outlet of the reverse osmosis racks varies from 5.3 to 6.7 and the CO_2 content ranges between 0.8 and 16 mg CO_2/L, depending on plants.
6. The corrosivity indexes suggested that the desalinated waters tend to dissolve calcium carbonate. This also implies the risk of problems of corrosion due to higher chlorine (60–200 mg Cl^-/L) and sulphate content (2–5.7 mg SO_4^{2-}), with respect to the content of hydrogen carbonates (2–4 mg HCO_3^-/L).
7. The pH of desalinated water quickly balances with the CO_2 content of the atmosphere which results in loss of CO_2. Therefore, pH should be analyzed carefully "in situ". So the pH and the CO_2 content of desalinated water depend to a large extent on the pretreatment of RO.
8. Data collected from the 6 plants showed that none of the waters of the studied plants comprise enough CO_2 at the racks outlet to complete a re-mineralization process properly.
9. In equilibrium with the atmosphere, the pH of osmotic water is around 6.9–7.0 and CO_2 content around 0.3 mg CO_2/L. The LSI remains at around −4. (e.g. if stored during overnight, the pH will be around 5.6, reaching the pH of pure rainwater.)
10. The average value of SAR (sodium adsorption ratio) is around 9, which may cause damage to soil structure and crops. For this reason, re-mineralization or addition of Ca and Mg directly with fertilizers should be done in order to prevent this damage.
11. For future re-mineralization, humans' need for minerals from drinking water should be regarded.

6.1.2 Hardness and Alkalinity

The water assessment criteria used for continental waters can also be applied for desalinated water and re-mineralized water. The total hardness (TH) is defined as the sum of concentrations of calcium and magnesium. In desalinated water and

Table 6.1 Assessment of water hardness in mg $CaCO_3$/L

Assessment of the hardness (mg $CaCO_3$/L)		Assessment of the alkalinity (mg HCO_3/L)	
<17.1	Soft	<12.3	Very low
17.1–60	Slightly hard	24.6–41	Low
60–120	Moderately hard	41–98.4	Medium
120–180	Hard	98.4–147.6	High
>180	Very hard	>147.6	Very high

re-mineralized waters, alkalinity relates to the presence of hydrogen carbonates and carbonates. In the case of desalinated water, the non-carbonated Ca and Mg are combined with chloride and sulphate anions. Table 6.1 describes the assessment of water through hardness and alkalinity.

6.1.3 Saturation and Langelier Index

Langelier Saturation index can be used to calculate if the water is saturated with limestone, i.e. if $CaCO_3$ will precipitate at actual pH. The established saturation index is:

$$LSI = pH - \mathrm{pHsat}$$

where:

pHsat: saturation pH is the theoretical value at which the solution would be saturated with calcite under conditions of chemical equilibrium in which the calcite neither dissolves nor precipitates. The calculation of pHsat is through either a simplified graphical method or a more rigorous calculation (see, for instance, the Spanish Standard Method 2330 (SM2330), www.fcca.es=>Software).

Through comparison with the above two methods, we can conclude that both calculation of pHsat and LSI by a simplified method is 0.2 units lower than SM2330. It is recommended to use SM2330, which is the internationally adopted method to comply with EU regulations.

6.1.4 Larson–Skold Index

Larson–Skold Index is an indicative check to see if the water has the potential for pitting corrosion of copper. This is calculated through:

$$LaI = \left(\left[CL^{-}\right] + \left[SO_4^{2-}\right]\right) / \left(\left[HCO_3^{-}\right] + \left[CO_3^{2-}\right]\right)$$

where:

LaI >1.2 high degree of corrosion;
0.8 <LaI <1.2 Significant degree of corrosion;
LaI < 0.8 No risk of corrosion
All concentrations in mg/L

6.1.5 DIN Standards

There are a number of German industrial Standards such as DIN 4046 and DIN EN 12502 which relate to the capacity of water to dissolve calcite and to the risks of corrosion for different materials. DIN 50930 is similar to the Larson-Skold Index and applied in certain cases at the international level (Table 6.2). This standard establishes the value of "S" as follows:

$S = ([Cl^-] + 2[SO_4^{2-}])/([HCO_3^-])$ and it recommends $S < 1$ to minimize the risk of corrosion due to pitting.

6.1.6 SAR (Sodium Adsorption Ratio)

SAR of water is as reflected in the following formula:

$SAR = Na^+/ ((Ca^{2+} + Mg^{2+})/2)^{0.5}$ (Unit of Ca^{2+} and Mg^{2+}: meq/L)

6.1.7 Optimum Re-mineralization Level

Re-mineralization is performed through a set of technologies to increase the hardness and alkalinity of water to achieve the Langelier Saturation Index equal or very close to zero and keep the water in stable contact with the atmosphere. Also, this process should be optimized accurately though analysis processes in order to

Table 6.2 SAR (Sodium Absorption Ratio) assessments

SAR	Assessment
SAR >12	Very important damage
9 < SAR < 12	Important damage
6 < SAR < 9	Growing problems
5 < SAR < 6	Initial Problems
3 < SAR < 5	Low risk
1 < SAR < 3	No risk

Table 6.3 Recommended technical characteristics for desalinated waters in an optimum re-mineralization level (for corrosion control)

Parameters	Range
pH	8.2 ± 0.1
Alk, mg $CaCO_3$/L	56 ± 3
HCO_3^-, mg/L	68 ± 3
Ca^{2+}, mg/L	21 ± 2
CO_2, mg/L	0.7 ± 0.1
LSI (SM2330)	±0.15

minimize the consumption of energy and chemicals, especially CO_2. Re-mineralized water should have typical characteristics as shown in Table 6.3.

The content of dissolved CO_2 is normally insufficient in desalinated water for proper re-mineralization. Therefore CO_2 needs to be added and transferred to alkalinity by addition of lime, limestone or lye. The dose of CO_2 required depends on the permeate alkalinity prior to re-mineralization.

The practical yield of carbon dioxide is 90–95% of added CO_2. Too low a dose of CO_2 produces water with low alkalinity, which may be acidified by uptake of CO_2 from the atmosphere, resulting in unstable water with a tendency to be corrosive. Too high a dose of CO_2 causes higher alkalinity and hardness in the re-mineralized water that may result in CO_2 loss to the atmosphere, causing pH to increase and thus a slightly positive LSI. The CO_2 content in water which is in equilibrium with the CO_2 in the atmosphere naturally defines pH and the combination of carbonates and hydrogen carbonates corresponding to this pH.

If further pH elevation is needed, it can be realized by NaOH dosage, as practiced, for example, in Kuwait (Alrqobah et al. 1989) and Qatar (Migliorini and Meinardi 2005). When dissolution of $Ca(OH)_2$, $CaCO_3$ or $MgO*CaCO_3$ (dolomite) together with Na_2CO_3 or $NaHCO_3$ is performed, using CO_2 as acidifying agent, excess CO_2 may be emitted, thus increasing the pH value (Birnhack et al. 2011).

The most widely used re-mineralization techniques such as calcite bed and lime slurry are both highly developed. The advantage with calcite or dolomite bed filtration is that less CO_2 is consumed and the operation is easier compared to lime slurry. To adjust the relation between calcium and magnesium, it is possible to mix different calcite and/or dolomite materials, with different proportions of Ca/Mg. Dolomite limestone has a higher content of Mg than ordinary calcite. Using dolomite limestone in the re-mineralization process will give the treated water a higher Mg/Ca ratio.

If calcite or dolomite bed is used for filtering material, the material purity is around 99%, normally with a grain size of around 1–4.3 mm, however 1–3 mm is preferred. The filtration beds are installed in filters that are either open or closed under pressure, and both filtering directions, i.e. up flow and down flow, are possible. In general, it is necessary to do backwashing every 10–14 days. It is also recommended that the height of the filtering layer be between 1.5 and 3 m and a filtering velocity between 10 and 16 m3/h is generally applied. The dose of CO_2 should be operated in down flow with a descending speed of about 0.07 ± 0.02 m/s, avoiding use of horizontal pipe, in order to prevent the drag of bubbles and over-dosage. Temperature decrease reduces the speed of the reactions, slowing down the re-mineralization process. For the application of calcite beds, a decrease in temperature from 28° C to 14° C will require a contact time in the range of 10–14 mins. Calcite and/or dolomite is consumed in the process and must therefore be added regularly in order to maintain the correct level of material in the filters.

The risk of precipitation of $CaCO_3$ is low as long as the LSI is between 0.5 and 1.0, even at the temperature of 40 °C.

Slaked lime ($Ca(OH)_2$) can also be used for re-mineralization. Lime is dissolved or suspended in water to produce lime water or lime slurry. After addition of carbon dioxide, the pH is set by addition of lime. When using slurry, sufficient time for dissolution must be applied to avoid post-treatment sediments in reservoir and pipes. This method presents fewer disadvantages than the other methods. This method enriches the water with both total hardness and alkalinity (at a 1:1 ratio, in equivalent units). The most frequent challenge with the operation of such re-mineralization systems is to maintain low turbidity in final drinking water, because lime can cause a turbidity increase, often exceeding 5 NTU. Moreover, the use of the hydrated lime slurry is relatively complex from the engineering point of view, especially if the permeate is warm. This reduces the solubility of lime from 1.73 g/L at 20 °C to 1.40 g/L at 40 °C.

The limestone process presents a few disadvantages. Its reaction is much slower and does not reach completion, so that residual excess CO_2 has to be neutralized by the addition of NaOH or Na_2CO_3. Another difficulty, in the design of the limestone dissolution beds, is the lack of reliable data on the kinetics of dissolution of limestone by CO_2-acidified water. Tests need to be performed in order to learn how the specific water of a plant will dissolve limestone.

The use of sodium hydrogen carbonate and calcium sulphate is less common in re-mineralization applications due to the low solubility of calcium sulphate in water (0.23% by weight) and the high cost of sodium hydrogen carbonate. Both materials tend to form cakes when stored or used in humid conditions. In some plants $CaCl_2$ in combination with $NaHCO_3$ is used for re-mineralization. In a recent study from Singapore, the researchers conclude that Ca^{2+}+Mg^{2+} combination improves the chemical stability of desalinated seawater rather than Ca^{2+} only. Ductile iron, cast iron and cement-lined ductile iron were explored to remineralized reverse osmosis (RO) membrane desalinated seawater. The best combination was 60 mg/L Ca, 40 mg/L Mg and 100 mg/L HCO_3 (Liang et al. 2014). Re-mineralization was more efficient in a fluidized bed reactor than in a fixed bed reactor (Luptáková and Derco 2015).

Sodium carbonate is also costly and less common in re-mineralization applications. It is useful when the water has appropriate hardness but too low alkalinity. The use of online micronized lime appears to be an interesting way to remineralize aggressive water. The product is called micronized $CaCO_3$ slurry. Natural limestone has been the ground to produce fine particles (1–2 μm) with a high specific surface area. It is dosed directly in the water as concentrated slurry. The main advantage of this method is that the online use of micronized lime does not degrade over the turbidity of water produced as lime water prepared classically, while allowing identical re-mineralization.

If a low-cost source of CO_2 is not available (e.g. treated power station exhaust gas), using a strong acid such as H_2SO_4 is a less costly and simpler practice, since pressure tanks are not needed. The main advantage is the rapid dissolution that can be attained when a strong acid is introduced to water. Thus, it is possible to dissolve a significant amount of calcite in water that passes through the reactor, and let the majority of the flow, between ~70% and ~85% of the total flow rate of the plant (in case the product water alkalinity should be ~32 mg/L Ca), bypass the reactor, a fact that renders the reactor considerably less costly (Birnhack et al. 2010).

6.1.8 Blending Waters

If other freshwater sources are available, desalinated water can naturally be blended with freshwater to produce re-mineralized mixed water. This is applied in many plants in the world. When blended, the quality and chemistry of the mixed waters must be recognized and the mixed water composition maintained at constant conditions. The producer must keep an even quality (with LSI equals 0) without an LSI value less than −0.5. Mixing programmes such as Water-Pro and Softmix are available for simulation (see websites: http://chemsw.com and http://www.fcca.es). The model calculations should be validated with laboratory analysis.

During a visit to Saudi Arabia in January 2017, researchers from Sweden (Ingegerd Rosborg and Kenneth M Persson) met researchers from Saudi Arabia for future cooperation between the two countries. The hardness as measured with a hardness kit, including EDTA and Erio-T indicator, showed hardness 0 at a hotel, but 10 °dH at a university. The hotel obviously performed total softening or RO-treatment of the water. However, the public water was a mixture of RO water with extremely mineral-rich groundwater, from sandstone bedrock, with a final total hardness of around 10 °dH. Professor Radwan Alrasheed, The King Abdulaziz City of Science and Technology (KACST), Riyadh, Saudi Arabia, declared that even water for future irrigation was aimed to be mineral rich.

In countries, or certain areas in the world, drinking water often is produced from low-mineral rain-like surface waters, such as Finland, Norway, Sweden, Switzerland, and Canada. Surface water is used in 50% of the production of drinking water in Sweden. Most lakes are located on primary rock bedrock, gneiss and granite, and thus have low levels of minerals (Fig. 6.1). However, a few are located in limestone bedrocks and thus have mineral-rich water (Fig. 6.2).

Fig. 6.1 Swedish lake located on primary rock bedrock, gneiss and granite, spruce and pine (Svahn PE 2014, e-mail comm.). This kind of lake has highly mineral-poor water

Fig. 6.2 Swedish lake located on lime-rich slate bedrock (photo: Nihlgård B). This kind of lake has highly mineral-rich water

6.2 De-mineralization/Desalination

A. Brenner, I. Rosborg and F. Kozisek

Due to the increasing problems of water shortage across the world, the trend since the 1960s has been for producing new water sources by de-mineralization/desalination of seawater and brackish water (Fig. 6.3). First, distilled water was used and now deionized or reverse osmosis-treated (RO) water is often produced for industrial, technical and laboratory purposes, and for ocean-going ships and spaceships. There are more than 21,000 desalination plants around the world providing more than 350 million people with drinking water. In the Middle East and Western Asia, more than half of the drinking water is produced in this way. In South Korea, 80% of the population consume only RO water (IMBC 2012).

Desalination converts water with high total dissolved solids (TDS) content into water with very low dissolved solids content, and also removes impurities, such as residual organics and microorganisms. Reverse osmosis (RO) is the most common process applied today in the desalination of seawater or brackish water for drinking water supplies. While osmosis is a natural phenomenon of water diffusion through a semi-permeable membrane, which occurs due to a concentration gradient (the direction of water is from the low solute concentration to the high solute concentration), reverse osmosis requires input of an external pressure to drive the flow in the opposite direction (Crittenden et al. 2012). Worldwide, bottled water is increasingly used for drinking, since it is regarded “clean” and “safe”. However, a lot of them are treated with RO (reverse osmosis) (Fig. 6.4). For health effects related to drinking RO water, see further Chap. 7.

Fig. 6.3 Desalination plant (RO) in Stockholm archipelago (photo: Alm J 2014)

Fig. 6.4 Some brands of bottled waters in a fridge in GBR Berlin (Reimann and Birke 2010)

Nano-filtration (NF) is a more moderate lower pressure driven process in which monovalent ions pass freely through the NF membrane, while highly charged multivalent salts are rejected due to the special structure of the NF membrane surface that is negatively charged at neutral and alkaline media. The main advantage of this process is the possibility to achieve high ion rejections at relatively high permeate fluxes, which is very important from a practical point of view as more water can be produced at a lower capital cost. Typical NF applications include water softening (Nanda et al. 2008).

For these two processes, the separation is based not only on physical mechanism related to membrane pore size (relatively small) that serves as a barrier, but also on the chemical structure of membrane material that can dissolve, attract or reject various substances. In addition to the production of potable water from salt and brackish water, there are other uses of technologies focused on removal of specific elements: softening, natural organic matter removal for disinfection, by-products control and specific contaminant removal such as heavy metals, radio-nuclides or emerging micro-pollutants (Landaburu-Aguirre et al. 2006).

Electrodialysis (ED) belongs to the desalination processes, because of its ability to separate ionic substances. However, it is driven by an electrical potential and is limited to partial rejection of monovalent and divalent salts and of dissociated acids (Van der Bruggen et al. 2004).

6.3 Softening

I. Rosborg

The issue with low-mineral drinking water is also relevant when softening is practiced (Rosborg et al. 2005). Among the substances present in water, hard water minerals, such as salts of Ca and Mg, may cause scaling problems in boilers, heat exchangers and electrical appliances, such as washing machines, dishwashers and steam irons. Other troubles of hard water include higher consumption of detergents, and aesthetic problems related to the appearance of scaling products on clothes and glass (VAV 2010) (Fig. 6.5).

Hardness is expressed in terms of the total concentration of Ca and Mg, “Total Hardness”, or mg/L as $CaCO_3$, or just Ca. Hardness can be further classified into carbonate and non-carbonate hardness. Carbonate hardness is the product of dissolution of Ca or Mg carbonate and hydrogen carbonate in water. Non-carbonate hardness is contributed by compounds of Ca or Mg with sulphate, chloride, or silicate. Over the last 150 years, several classifications of water hardness have been developed. One type of grading is shown in Table 6.4, and is often expressed in °dH, “German degrees”, where 1°dH corresponds to 10 mg/L CaO or 7.1 mg/L Ca or/and 4.3 mg/L Mg (VAV 2010).

If the hardness is removed by ion-exchange filters, NaCl is added (salt solution is stored in the white container in Fig. 6.6), and the Na concentration increases, as the cations Ca and Mg are exchanged for Na.

Fig. 6.5 Lime scaling in water pipe (MERUS 2014)

Table 6.4 The grading of hardness as mg/L $CaCO_3$, Ca and °dH, "German degrees", respectively (VAV 2010)

Hardness	$CaCO_3$ (mg/L)	Ca (mg/L)	°dH
Very soft	0–32	0–14	0–2
Soft	32–80	14–35	2.0–5.0
Moderately hard	80–160	35–70	5.0–10.0
Hard	160–320	70–140	10.0–20.0
Very hard	>320	>140	>20

Fig. 6.6 Softener, ion-exchange filter, in a residential community in Sweden (Photo: I Rosborg)

In one case study on an island in the Stockholm archipelago, Sweden, one of the residents in a water community had problems with scaling in a pipe between the tap and a jar in the refrigerator. A softening filter was installed. Total softening was performed. Residents could not get rid of shampoo and soap because of the total softening. An extensive water analysis was performed after passage of the filter, see Table 6.4. Ca and Mg were almost completely removed, as hardness was decreased from 10 °dH to below the detection limit, 0.15 °dH. Na was increased, and uranium (U) was preserved, 15 µg/L. Since the antagonistic and protective mineral Ca now was almost eliminated, the U posed an increased health hazard. Uranium in drinking water may have negative effects, especially on kidneys (Kurttio et al. 2002) (Table 6.5).

When chemical precipitation is applied to remove water hardness, addition of hydroxide ions (to raise the pH above 9), most commonly done with lime ($Ca(OH)_2$), but also with NaOH, is sufficient to remove the carbonate hardness. Removal of

Table 6.5 Analysis of drinking water in a residential community of Sweden in 2011

	Water before ion-exchange filter	Water after ion-exchange filter
pH	8.2	8.3
Conductivity (mS/m)	45.6	43
Hydrogen carbonate mg/L	160	150
Turbidity FNU	0.14	<0.1 (det.limit)
COD (Mn) mg/L	1.1	1.0
Tot. hardness °dH	10	<0.15 (det.limit)
Calcium mg/L	62	0.33
Magnesium mg/L	5.9	<0.5 (det.limit)
Sodium mg/L		89
Potassium mg/L		<0.1 (det.limit)
Iron mg/L	<0.05 (det.limit)	<0.020 (det.limit)
Manganese mg/L	<0.02 (det.limit)	<0.010 (det.limit)
Copper mg/L	0.01	0.037
Aluminium mg/L	<0.02 (det.limit)	0.002
Nitrate mg/L		1.4
Nitrite mg/L	<0.003	<0.007 (det.limit)
Ammonium mg/L	<0.02 (det.limit)	<0.010 (det.limit)
Fluoride mg/L		0.43
Chloride mg/L		30
Sulphate mg/L		41
Phosphate-P mg/L		<0.020 (det.limit)
Silicon mg/L		5.6
Silver μg/l		<0.1 (det.limit)
Arsenic μg/l		<0.2 (det.limit)
Boron μg/l		23
Barium μg/l		<1 (det.limit)
Beryllium μg/l		<0.1 (det.limit)
Cadmium μg/l		<0.02 (det.limit)
Cobalt μg/l		<0.2 (det.limit)
Chromium μg/l		<0.2 (det.limit)
Lithium μg/l		<50 (det.limit)
Molybdenum μg/l		1.4
Nickel μg/l		3.1
Lead μg/l		1.2
Rubidium μg/l		0.6
Antimony μg/l		<1 (det.limit)
Selenium μg/l		<0.5 (det.limit)
Tin μg/l		<0.1 (det.limit)
Strontium μg/l		<1 (det.limit)
Titanium μg/l		<50 (det.limit)
Uranium μg/l	15	15
Vanadium μg/l		<0.2 (det.limit)
Zinc		30
Zirconium		<0.1 (det.limit)

non-carbonated hardness requires the addition of soda ash (Na_2CO_3). These additions cause precipitation of Ca salts. Similar phenomenon occur when ion-exchange resins serve for hardness removal, since Na (or K) ions replace Ca and Mg, and Na (or K) is released into the water (Heidfors 1992).

In a Swedish city, Uppsala, softening has been performed for some years in order to decrease scaling, but also to decrease the U concentration, which was above the WHO guideline value 30 µg/L, highest 60 µg/L. Thus, Ca decreased from above 80 mg/L to less than 40 mg/L, Mg from 28 mg/L to around 15 mg/L. However, U concentration still is high; average just below 30 µg/L, and range 16–33 µg/L. Since Ca is the most important U-antagonist, and now is present to a lower concentration, the protection against U is reduced.

In the Swedish study on municipal waters in South Sweden (Rosborg et al. 2005), softening filters in hard water on limestone bedrock produced water with Ca concentrations comparable to the softest waters from primary rock bedrock. Ca concentrations were around 70 mg/L before softening and less than 20 mg/L after softening.

6.4 Other Filters and Treatment Devices, Municipal and Private

I. Rosborg

Filter aimed for reduction of specific substances may alter concentration of other elements and ions, as well (Rosborg et al. 2005).

6.4.1 Sand Filter

Sand filtering is often performed at especially public surface water plants to clear the water from large impurities. In the Swedish study on municipal waters in South Sweden the concentration of Cu and Zn were significantly higher in sand filter-treated drinking water when compared to raw water. The reverse pattern was observed for the concentrations of Mn. The increased concentrations of Cu and Zn in treated waters probably originate from the sand, since pipes were consistently made of stainless steel in the water plants (Rosborg et al. 2005).

6.4.2 Iron and Manganese Filter

When Fe and/or Mn are present in raw water at elevated concentrations colouring in clothes and sanitary ware causes problems, also color and turbidity of water may be compromised. pH and the concentrations of Cu and Na, HCO_3 and NO_3 were higher in such treated municipal drinking water, while the levels of Ca, Fe and Mn were lower (Rosborg et al. 2005).

6.4.3 Softening Filter

Deposits of Ca and/or Mg salts are common in pipes and installations when the water is hard. In ion-exchange filters Ca and Mg are replaced for Na as NaCl is present in the ion-exchange resin binding sites and Ca and Mg in the water will be exchanged with Na. At some plants, the concentrations of Cu was increased after filtering. Na was always higher after passage of ion-exchange filters, while the concentrations of Ca, Fe, K, Mn and U were lower (Rosborg et al. 2005). Also, supplementation with NaOH in order to precipitate $CaCO_3$ and $Mg(OH)_2$ can be performed.

In another kind of ion-exchange filter, there is an ion-exchange mass of e.g. the polymer sulphonated polystyrene. The polymer binds Na-ions peripherally, which can be exchanged for Ca and Mg ions in passing water. The water becomes soft or even completely free of Ca and Mg. Na accompanies the water. Some of the water can be shunted past the filter, resulting in partially softened water, which is better from corrosion and health points of view. Upon regeneration of the filter, Na-ions are supplied in the form of NaCl. The filter must be flushed before regeneration to remove formed sludge. If the raw water has high Fe and Mn levels, these must be reduced first to avoid precipitation in the curing filter. softening should not be performed to hardness levels <6-8 ° dH, to avoid corrosion and keep acceptable mineral levels, Ca and Mg (editor's comment).

6.4.4 Filter with Chemical Precipitation

When humic acids are present in raw water, chemical precipitation is performed, where generally polyaluminium hydroxychloride and calcium hydroxide, $Ca(OH)_2$, are added. Iron chloride, $FeCl_3$, can also be used. Then various pollutants are captured in the formed precipitation flocks. In the Swedish study, pH, conductivity and the concentrations of Ca, Cl and HCO_3 were increased, while the levels of Al, Cu, Fe, Mn, Pb, Se, TOC, U and Zn decreased significantly by this treatment (Rosborg et al. 2005).

6.4.5 Supplementation with NaOH to Increase pH

At some water plants in the Swedish study, NaOH was supplemented to increase the pH value. Thus pH, conductivity, HCO_3 and Na increased due to the supplementation with NaOH, while Mn, Ca, Fe and Pb decreased significantly (Rosborg et al. 2005).

6.4.6 Supplementation with $Ca(OH)_2$ to Increase pH

At water plants where $Ca(OH)_2$ was supplemented to increase the pH value, conductivity and the concentrations of Ca and HCO_3 increased significantly, as well as Na, K and Cl. On the other hand the concentrations of Al, Fe, Mn, TOC, Pb and Zn decreased (Rosborg et al. 2005).

6.4.7 Carbon Filter

Carbon filters are used to reduce organic substances, such as solvents and pesticides. The organic substances stick to the carbon particles. Even humic substances are reduced by carbon filter. Solid block activated carbon (SBAC) filters remove 80–99% of total Pb and 68–98% of total Cu. SBAC remove multiple categories of pollutants, including metals, VOCs and particles (Ward Brown et al. 2017).

6.4.8 Membrane Distillation

In membrane distillation, hydrophobic membranes are used to separate pure distillate water from warm water. Water vapour is transported through the membrane due to a pressure difference caused by the difference in temperature. This process of evaporation and condensation cools the hot side and heats the colder side. The process works at low pressures (as low as 1.0 bar). Water like rainwater or distilled water is produced.

6.4.9 Nitrate Filter

This is generally an ion-exchange filter, where zeolite or synthetic resins are used. The water is allowed to pass through a bed of ion-exchange resin, where nitrate (NO_3^-) is replaced with chloride (Cl^-). Regeneration of the filter is done with NaCl. Available knowledge does not indicate that this process would change levels of essential elements, with exception of chloride. RO is not recommended for elimination of nitrate, since it totally de-mineralizes the water, producing water similar to rainwater or distilled water.

6.4.10 *Fluoride Filter*

The filter in general contains alumina, Al_2O_3, which precipitates the fluoride. The filter mass is replaced periodically, as the fluoride becomes solid in it and must be removed so as not to enter the water again. Nano-filtration can also be used (Singh et al. 2016). However, there are more methods used for this purpose. Thus, filtration methods recommended by the EPA (United States Environmental Protection Agency) and the WQA (Water Quality Association) are: Bone Char Filtration, Ion-Matrix Filtration, Activated Alumina Filtration, Reverse Osmosis Filtration, and Distillation (US EPA 2018). RO and distillation indeed affect mineral concentrations. Since these methods totally de-mineralize the water, producing water similar to rainwater or distilled water.

6.5 Experiences of Desalinated Seawater from Israel

A. Brenner

As discussed before, water production and treatment processes can affect the mineral content and balance, and increase or decrease the contribution to the total intake of essential minerals for some individuals. If desalinated water is blended with raw saline water, it can regain its original mineral balance in a moderately acceptable manner. This is common practice in small desalination plants, especially those plants that use brackish water. For large seawater desalination plants, stabilization is a mandatory practice (for corrosion control purposes) based commonly on the dissolution of $CaCO_3$. This technology (sometimes termed calcification) can actually supply the required levels of alkalinity and Ca to minimize corrosion. The added Ca will also serve to account for part of the dietary portion of Ca that can be obtained from drinking water. However, this technology does not supply sufficient Mg, and the ratio of Ca to Mg, following desalination-calcification, becomes very high and may not enable efficient absorption of Mg (unless Dolomite is used as the stabilization mineral) (Tang et al. 2006).

Re-mineralization experiments of RO water in Israel with calcite increased concentrations of some elements and ions from almost 0 to levels presented in Table 6.6.

Ag, As, Ba, Cd, CN, Cr, Hg, Ni, Pb, Se, Cu, Mg, Mn, Zn, F, NH_4 and NO_3 were also analysed. However, after re-mineralization of these elements and ions their levels were below the detection limits. The concentration of Mg was not increased. In order to acidify the water aimed at Ca dissolution (calcification), CO_2 was added in one of the plants, and H_2SO_4 in the other active plants (Fig. 6.7).

New standards for desalinated water have been recently issued by the Israeli Ministry of Health and are presented in Table 6.7.

Regarding the Mg issue, the WHO (2009) details many published studies concerning the beneficial health effects of Ca and Mg. Despite the relatively low potential contribution from drinking water supplies, compared to food sources, obtaining the potential portion present in water supplies should be seriously considered, as

Table 6.6 Concentrations of elements and ions that increased during calcite re-mineralization in the Israeli desalination plants (Israel Ministry of Health, unpublished data)

	After re-mineralization	Unit
SO_4	13–57	mg/L
pH	7.4–8.9	
Al	0–8	µg/L
Fe	0–6	µg/L
Alkalinity	39–83	mg/L CaCO3
K	0–1.3	mg/L
EC (conductivity)	209–396	µS/cm
Na	6–38	mg/L
Ca	35–38	mg/L
Hardness	82–90	mg/L CaCO3
Cl	7–49	mg/L
Turbidity	0.1–0.2	NTU
HCO_3	61–101	mg/L
TDS	104–225	mg/L

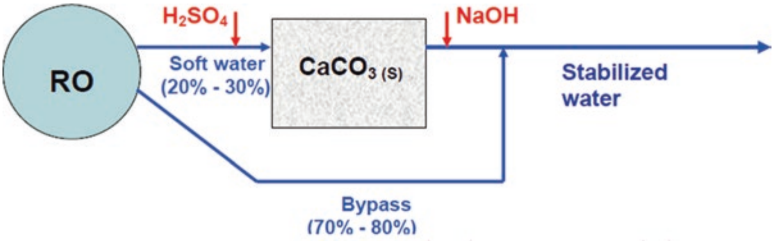

Fig. 6.7 Typical calcification of RO-treated water in Israel

can be concluded from the many studies that have been conducted to date around the world. There is still a debate in Israel regarding the addition of Mg to desalinated water. In this regard, to solve the problem of Mg deficiency, a unique post-treatment aimed at supplying a balanced concentration of alkalinity, Ca, Mg and SO_4, has been proposed for desalinated water (Whiting and Wood 1997; Birnhack and Lahav 2007).

The process is based on replacing excess Ca ions generated in the common H_2SO_4-based calcite dissolution process with Mg ions separated from seawater by means of a specific ion-exchange resin. This process can be adjusted to control pre-determined desired concentrations and Ca:Mg ratio. Another alternative post-treatment process to restore both Ca and Mg in desalinated water, based on combined in-series dolomite-calcite dissolution has also been proposed (Birnhack et al. 2009). However, it has been found to be more complicated and costly than the previous technology, and the resulting water total hardness value is high.

Mineralization by adding limestone to acid well water, with very low concentrations of minerals, increased the Ca level to around 10–15 mg/L (Rosborg et al. 2002).

Table 6.7 Quality standards for desalinated water in Israel (Brenner and Tenne 2010)

Monitoring	Monitoring location	Parameter	Units	Maximum concentration
Continuous	Exit of desalination process	Conductivity	µS/cm	95% of daily values < OV and not higher than 1.3(OV)[a]
	Exit of calcification process	Turbidity	NTU	95% of daily values <0.5 and not higher than 1.0
		pH		7.5–8.3 in 95% of daily values and not higher than 8.5
Batch	Exit of calcification process	Dissolved Ca^{++}	mg/l as $CaCO_3$	80–120
		Alkalinity	mg/l as $CaCO_3$	> 80
		CCCP[b]	mg/l as $CaCO_3$	3–10
		LSI[c]		> 0

[a] OV=Operational Value, approved by Health Authorities (specific to each plant). OV is a specific and different value (of water conductivity) set for each desalination plant. The values range between 200 and 400

[b] Calcium carbonate precipitation potential

[c] Langelier Saturation Index

Table 6.8 Proposed optimum concentrations in Israel after re-mineralization (Birnhack and Lahav 2007)

Parameter	Proposed optimum (mg/L)
Ca	40–50
Mg	>10
F	0.5–1
Hardness	<150 (as $CaCO_3$)
TDS	≈200

In Israel also, optimum levels of minerals after re-mineralization were proposed; Table 6.8.

An acceptable ratio between Ca and Mg, Ca:Mg = 4–5:1, is achieved, which is very important in the balance between minerals, even if the ratio is larger than the suggested ratio of 2–3:1.

6.6 Rainwater Harvesting

I. Rosborg

Rainwater harvesting for drinking water purposes is increasingly done in arid areas over the world. In an Australian study, the opposition to chlorinated and fluorinated drinking water was high among citizens. For that reason, in addition to limited community drinking water, rainwater harvesting was applied among citizens (Chubaka et al. 2017). Overall, about 10% of Australian households use rainwater as their main source of drinking water at home. Pure rainwater is completely without minerals. There is no study revealing the health impact of this practice (resulting in drinking water low in minerals), so far.

6.7 General Advice Before Choice of Treatment Process

I. Rosborg

A treatment process that preserves or improves the mineral content/balance should be chosen.

In summary:

- Softening to avoid scaling on pipes and installations should not decrease the hardness to levels below 6–8 °dH.
- Alkaline filters used to increase pH for corrosion purposes should not be performed by adding NaOH, since only Na and the alkalinity (only slightly) is raised. Dolomitic limestone is preferable.
- In water with the presence of toxic metal(s) the concentrations of the protective (antagonistic) elements should be as close to the upper limit of the suggested intervals as possible. Thus, in water with, e.g., Pb or U, softening should not be performed to a lower level than 6–8 °dH.
- RO-treated water should always be remineralized to at least the lowest concentrations in the suggested interval, for a number of elements, especially Ca: 30 mg/L, Mg: 10 mg/L, HCO_3: 100 mg/L and SO_4: 25 mg/L, or blended with mineral-rich water.

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Chapter 7
Health Effects of De-mineralization of Drinking Water

Ingegerd Rosborg, Frantisek Kozisek, and Margherita Ferrante

Abstract Desalinated water, mainly RO, but recently also produced from air humidity by condensation, is extremely low in minerals, comparable to rain water or distilled water, and even when pH-adjusted such water has low mineral content. Reduced mineral intake, due to drinking de-mineralized water, is not automatically compensated by one's diet. Especially not since there are scientific studies that show decreasing levels of a number of essential minerals in vegetables. Animal studies showed that mean haemoglobin content of red blood cells was approximately 19% lower in animals receiving non-supplemented de-mineralized water compared to animals given tap water. Higher mortality in acute myocardial infarction patients was found in regions where the drinking water was desalinated water, attributed especially by reduced magnesium intake. "Water intoxication", or delirium caused by hyponatraemia, may occur following intense physical efforts, like a marathon or working hard, and ingestion of several litres of low-mineral water. Early symptoms include tiredness, weakness, headache, brain oedema, convulsions and in severe cases coma and finally death. Electrolyte imbalance, hyponatraemia, hypokalaemia, hypocalcaemia and hypomagnesemia are the most common co-morbidities in cancer patients, which underlines the importance of minerals from drinking water. Declining dental health was reported in populations consuming desalinated water, due to low Ca and F levels in water. Drinking low-mineral water in the long run will increase the risk of acidosis, acidified tissues, as indicated by pH < 6 in urine. Thus, metabolic acidosis was reported in infants whose drinks were prepared from distilled or low-mineral bottled water. Acidosis may be a precursor to

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many diseases, e.g. cardiovascular diseases, diabetes, osteoporosis and cancer. Minerals in water are also needed to prevent corrosion and dissolution of pipe material, which makes the water unhealthy, and they are also needed for partial protection against uptake or transportation in the body of toxic elements, e.g. lead (Pb) and uranium (U).

Over 21,000 desalination plants operate in more than 150 countries in the world, including Saudi Arabia, Oman, United Arab Emirates, Spain, Cyprus, Malta, Gibraltar, Cape Verde, Portugal, Greece, Italy, India, China, Japan and Australia. Worldwide, these produce more than 13.3 billion litres of potable water each day, and provide 320 million people with drinking water. The capacity has increased exponentially over the last 30 years (Seawater Desalination 2018). Such water is extremely low in mineral element concentrations. However, water without minerals is not found in nature except for unpolluted rainwater and naturally formed ice, even if many natural waters are low in many minerals or soft (low in divalent or multivalent cat-ions), and hard waters are often artificially softened, especially in industrialized countries. Low-mineralized water, with low concentrations of Ca, Mg and HCO_3, is unstable and can be more aggressive to piping materials. Such water more readily dissolves metals, such as Cu and Pb, and some organic substances from pipes, coatings, storage tanks and containers, hose lines and fittings (Brossia 2018).

Animal studies clearly show that reduced mineral intake, due to drinking de-mineralized water, is not automatically corrected by one’s diet. Kondratyuk (1989) reported that in a 6-month experiment on rats to evaluate the variation in the intake of microelements from drinking water there was an up to six-fold difference in their content in muscular tissue. Four groups of rats were given: (1) tap water; (2) low-mineral water; (3) low-mineral water supplemented with I, Co, Cu, Mn, Mo, Zn and F; and (4) low-mineral water supplemented with the same elements but at ten times those concentrations. The results indicated that the blood formation process was negatively influenced by non-supplemented de-mineralized water, as the mean haemoglobin content of red blood cells was approximately 19% lower in the animals that received non-supplemented de-mineralized water compared to that in animals given tap water, and the difference was even greater when compared with the animals given the mineral-supplemented waters.

The German Society for Nutrition warned the public against drinking de-mineralized water, and explained that water in the human body always contains electrolytes (such as K and Na) at certain concentrations controlled by the body. In addition, they stated that water resorption by the intestinal epithelium is also enabled by Na transport. Thus, if distilled water is ingested, the intestine has to take electrolytes from body reserves. Early symptoms of low electrolyte levels include tiredness, weakness and headache. More severe symptoms are muscular cramps and impaired heart rate. Thus, inadequate body water redistribution between compartments may compromise the function of vital organs (DGfE 1993). Ingestion of de-mineralized water leads to alterations in extracellular osmolality which can offset the osmoregulatory mechanisms: to maintain cell volume, ion transport, organic osmolyte concentration, protein structure, cell turnover, etc. (Kültz 2001).

Hyponatremic shock, "water intoxication", or delirium, may occur following intense physical effort and ingestion of several litres of low-mineral water (Basnyat et al. 2000).

Brain oedema, convulsions and metabolic acidosis were reported in infants whose drinks had been prepared with distilled or low-mineral bottled water (CDC 1994). Osmotic changes in blood plasma due to decreasing mineral concentrations resulted in the redistribution of body water, with an increase in the total extracellular fluid volume. In response to the changed plasma volume, there was an increase in Na elimination, and enhanced diuresis (WHO 1980).

There is currently no evidence to suggest that desalinated water can cause cancer. However, acidosis may influence molecular activities at the cellular level that promote carcinogenesis or tumour progression (Forrest Robey 2012). In addition, recent epidemiological studies show that heavy consumers of de-mineralized water with very low mineral content can create osmotic imbalance by losing huge amounts of Na, K, Ca, Mg and other trace mineral elements in urine, faeces and sweat, resulting in osmotic stress. In accordance, a large number of studies have reported that electrolyte imbalance, especially hyponatraemia, hypokalaemia, hypomagnesemia and hypocalcaemia are the most common comorbidities in cancer patients (Nriagu et al. 2016).

Declining dental health has been reported from populations consuming desalinated water with very low F content, as there was a moderate to high risk of dental caries (WHO 2005).

Brown et al. (2005) studied cardiovascular response in relation to drinking distilled (hypo-osmotic) water and 0.9% saline water (isotonic) among young healthy volunteers. They found that drinking an isotonic saline solution did not change heart rate, heart rate variability, baro-reflex sensitivity or total peripheral resistance in contrast to distilled water. Drinking distilled water, on the other hand, caused a series of cardiovascular changes, including increases in total peripheral resistance, cardiac interval variability and cardiovagal baroreflex sensitivity, and a decrease in heart rate (Brown et al. 2005). Series of studies from Taiwan suggested that regular intake of low mineral and soft water increases the risk of some types of cancer (Yang et al. 1999a, b; Yang et al. 2000a, b), but possible mechanism was unknown until the study by Nriagu et al. (2016) was published. These studies should be taken more seriously, especially since this effect was confirmed by a large epidemiological study in another country, Slovakia (Rapant et al. 2015, 2017a, b). Fresh water from the Israeli National Water Carrier (NWC) is considered "hard", with concentrations of 45–60 mg Ca/L and 20–25 mg Mg/L, while desalinated seawater contains little or no Ca or Mg. Thus, in an Israeli study higher 30-day and 1-year all-cause mortality in acute myocardial infarction patients was found in the region with desalinated seawater compared to the region supplied with hard NWC water in the years 2008–2013. In the period 2002–2006, while they were still all drinking NWC water, there was no significant difference. The researchers concluded that this may be attributed to reduced magnesium intake secondary to desalinated seawater consumption. After 1 year, 95% had survived their acute myocardial infarction in the region with hard water, while about 90% had survived in the desalinated seawater area (Schlezinger et al. 2016).

In a Jordanian study, Ca intake from water was compared with total Ca intake. Sixty-three percent of the Jordanian people who live in Amman, 43% living in Irbid and 30% living in Zarqa depend on reverse osmosis (RO) water for drinking and cooking due to high salinity in tap water. The water contains no more than 6 mg/L Ca. Calculations showed that Ca intake where RO water was mostly used was less than the recommended amount. The authors concluded that if the reduction in Ca intake is not balanced in the diet, serious health problems such as osteoporosis may be the result especially in elderly people and women (Mousa et al. 2010). Between 2003 and 2010, the use of thyroid disease medication among Israeli adults increased from 2.9% to 4.7%, and during this time a large number of seawater reverse osmosis desalination plants were built along Israel's coast, eliminating almost 100% of iodine from drinking water. The Ashkelon desalination plant is the major source of drinking water in the Ashkelon District. Researchers obtained data on iodine status in adults in the Ashkelon district without reported or known thyroid disease. Results showed possible iodine deficiency ($Tg \geq 10$ μIU/mL) among 76% of the participants, which was higher than that reported a decade ago (Ovadia et al. 2013).

In addition to Ca and Mg, tap water and bottled waters may contain various concentrations of HCO_3, influencing the mineral homeostasis. HCO_3 is the main pH regulator in drinking water. Its importance is most probably underestimated, and can explain a big part of the pathologies resulting from drinking low mineral water. Thus, besides achieving the recommended amount of Ca and Mg in drinking water, a recommended level of 250 mg/L for HCO_3 has been suggested. As mentioned in Chap. 1, the net endogenous acid production is in close relation to excretion of both Mg and Ca (Rylander 2008).

In drinking water, pH alone is not the primary determinant of adverse effects on human health, since acids and alkalis are normally extremely dilute. Thus, although pH has no direct impact on the human body, it is one of the most important operational water quality parameters. The optimum pH will vary in different supplies according to water composition and to the nature of the piping materials used in the distribution system. However, Rosborg et al. (2002) stated that the mineral content was highest in the pH range 7–8, as minerals have been washed out from soils at low pH levels, and especially Ca salts tend to precipitate at pH exceeding 8. Because pH can affect the degree of metal corrosion, as well as disinfection efficiency, the authors (WHO 2005) declare that any effects on health is likely to be indirect and due to increased ingestion of metals from plumbing materials and pipes or due to inadequate disinfection, as well as due to low HCO_3 content resulting in higher Mg and Ca urinary losses, as mentioned above.

As discussed in connection with hard versus soft drinking water, the intake of soft water may increase the risk of cerebrovascular diseases (Yang 1998), fractures in children (Verd et al. 1992), certain neurodegenerative diseases (Jacqmin et al. 1994), pre-term birth and low weight birth (Yang et al. 2002), some types of cancers (Yang et al. 1999a, b, 2000a, b), death from cardiovascular diseases (Catling et al. 2008), increased risk of premature sudden death (Eisenberg 1992; Bernardi et al. 1995; Garzon and Eisenberg 1998), increased risk of motor neuronal diseases (Iwami et al. 1994; Melles and Kiss 1992), and pregnancy disorders (preeclampsia) (Melles and Kiss 1992).

Ca and, to a lesser extent, Mg in water and food are known to have antitoxic properties. They can help prevent the absorption of some toxic elements, such as, Pb, U and Cd from the intestine into the blood, either via direct reaction leading to the formation of an unabsorbable compound or via competition for binding sites (Levander 1977; Nadeenko et al. 1987; Kozisek and Rosborg 2008). Kozisek (2005) also states that populations supplied with low-mineral water may be at a higher risk in terms of adverse effects from exposure to toxic substances, such as Cu or Pb, compared to populations supplied with water of average mineralization and hardness, due to corrosion of pipe material. Although this protective effect is limited, it should not be dismissed.

The use of de-mineralized water also has effects on minerals from food. Losses of up to 60% of Ca and Mg have been reported when vegetables were boiled in de-mineralised water, and even more for some microelements; Cu: 66%, Mn: 70% and Co: 86% (Kozisek 2005). See the second box below for more information on this effect. In times when even former fertile areas are depleted of essential micro minerals like Se, Mo, Cr, Mn, etc. due to fertilization with only NPK (nitrate, phosphate and potassium), elements in vegetables and other plants also decrease, making drinking water minerals nowadays even more important than in the past. Since the 1850s, wheat has declined in Mg concentration by 7–29% in the USA and Mg in vegetables declined by 15–23% from the 1930s to 1980s (Rosanoff 2013).

The Armed Forces Medical Services (AFMS) of India declared: “As medical authorities we should advise and persuade administrative authorities to discourage tendencies of installing desalination/RO plants in the name of welfare or on demand of ill-informed clientele on the sake of “water fad” (without having scientific basis) to protect people from chronic diseases. The requirement of these should be assessed taking into consideration of geological parameters and chemical report of available water source in the area and be installed through authorized agencies with inbuilt mechanism for control, monitoring and evaluation of quality of processed water to safe guard health of the personnel in longer run”. (Verma and Kushwaha 2014).

Many schools in China introduced as preventive measure (to improve water quality) so-called direct drinking water systems that utilize reverse-osmosis (RO) – thousands of children are drinking, not as their choice, very low mineral drinking water. A recent Chinese study addressed the influence of regular drinking of such water on children’s health, especially on their development. Within an eco-epidemiological study, the authors collected developmental parameters of 13,723 girls and 16,161 boys before and after the introduction of RO drinking water systems in 25 schools and measured the mineral levels in water in each school. Water in 22 schools had lower than recommended levels of magnesium and calcium (Mg 10 mg/L and Ca 20 mg/L). The study found that children exposed to low-mineral water exhibited reduced height and diminished height increases as well as higher prevalences and incidences of hypoevolutism and dental caries with statistical significance. The results suggest that low-mineral water may retard height growth and promote the incidence of dental caries in schoolchildren and that the schools should choose another treatment system that retains the minerals in water (Huang et al. 2018). The follow-up case-control study involving 660 children confirmed that consumption of very low mineral water may be associated with osteoblast inhibition, bone resorption activation, bone mineral reduction, and height development retardation (Huang et al. 2019).

According to the study done in Qatar, pH-adjusted desalinated bottled water may cause deficiencies in nutrient mineral elements as it only accounted for 3% of the Institute of Medicine (IOM) Adequate Intake (AI) for Ca, 5–6% of the Recommended Daily Allowance (RDA) for Mg and 4% of the AI for F among adults. For children, desalinated water contributed 2–3% of the IOM AI for Ca, 3–10% of the RDA for Mg and 3–9% of the AI of F. On the other hand, Qatar's population is not at elevated risk of dietary exposure to As, Ba, Be, Cd, Cr, Pb, Sb and U from consumption of both desalinated and non-desalinated bottled water types available in the country (Rowell et al. 2015).

Case Studies of People with Health Problems After Drinking Osmotic Water: Experience from the Czech Republic

Information on single cases collected in a casual or informal manner and relying mostly on personal testimony, also called anecdotal evidence, have been considered for a long time as secondary information of limited value, not fitting in serious research. However, the times and our knowledge are changing and also use of anecdotal evidence gained its recognition and place in science. It was found, that some important information, e.g. about adverse effects of drugs and food products, is possible to get relatively quickly and effectively only in voluntary cooperation of consumers. That is why the specials reporting systems of adverse events have been developed and operated, e.g. FDA's Adverse Event Reporting System (FAERS) in the USA for drugs or Nutrivigilance in several EU member states for food products and dietary supplements.

We find similar situations in drinking water where quality was unusually changed (all total dissolved solids were removed), but not on the level of population supplied by municipal water supply, but on the level of single households. It would be very difficult to make any controlled epidemiological study – at least because it would be very difficult to get ethical approval if we know that a certain type of water treatment represents risk for health. That is why information on adverse health effects from people who bought and installed home water treatment device based on reverse osmosis or distillation in good will is very valuable to our knowledge on effects of low-mineral water on human health. Especially if more detailed information is collected from the consumers.

Awareness about health significance of nutrients in drinking water is quite common among professionals in public water and health in the Czech Republic (CR) since the 1960s, when the first studies on water hardness and

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health were published. This was reflected in recommended optimum values for hardness in the national standard for drinking water quality. Home water treatment units have been marketed and sold since 1990 in the CR, based solely on GAC, mechanical filters, or ion exchange (mostly for nitrate removal) until about 2000. Reverse osmosis (RO) units were used only for laboratory or various industrial purposes at that time.

Then in year 2000, several companies started to sell RO units also for home drinking water treatment. However, after only a few years proper regulatory framework was accepted and limited the use of RO units in a safe manner for consumers (see below). At this time dozens of people turned either spontaneously or on recommendation of the Regional Public Health Authorities to the National Institute of Public Health (NIPH) in Prague to share quite consistently their negative experiences after drinking water treated by RO. The NIPH was addressed in this issue by more than 50 people from the CR and some from Slovakia. The NIPH had the opportunity to study parts of these cases (24 people of 16 households) in more detail through directed interview or written questionnaire, water sampling, or results of laboratory analyses and several medical reports.

All these people were supplied with safe drinking water from public supplies. They bought the RO units because of unfair arguments of dealers that tap water is unsafe and not sufficiently monitored. All treatment units consisted 4 treatment steps: mechanical filter, GAU filter, RO membrane, and re-mineralization cartridge.

While drinking water supplied contained total dissolved solids (TDS) in the range 160–450 mg/L, Ca 25–103 mg/L and Mg 2–16 mg/L, water treated by RO units (even after "re-mineralization") had consistently negligible content of essential minerals: TDS 14–55 mg/L, Ca 0–7.2 mg/L (mostly less than 3 mg/L) and Mg 0–8.8 mg/L (mostly less than 1 mg/L).

All interviewed consumers, mostly middle age families with children with healthy lifestyle, started to drink water treated with RO with expectations to better protect their health, but sooner or later they started to have various health problems, although they were in most cases without any health problems before. The age range of cases that reported health problems was between 2 months and 66 years and the first signs of health problems appeared usually within several months after consumption of RO-treated water (on average 4 months, with a broad range; 2 days – 10 months). The reported health problems were extreme fatigue, malaise, nausea, headache, brittleness of nails and hairs, leg and abdominal cramps, pre-eclampsia and twitch, and in several cases also metabolic acidosis, cardiovascular disorders (arrhythmia, stroke, aneurysm), higher diuresis, leg oedema, giddiness and diarrhoea.

Some people complained about the taste of the treated water (no taste, unpleasant or strange taste, like chewing paper, not quenching thirst). When

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people realized that there was a relationship between their health problems and water quality, they stopped to drink the osmotic water and started to drink untreated tap or bottled water again, and in most cases health problems disappeared, but it took several weeks or months. Only some people needed medical treatment. NIPH also were informed about several deaths of people drinking osmotic water, but had no possibility to search for more details and causality.

In reaction to this situation, the public health authorities amended the regulation on products in contact with drinking water, which also covers home water treatment units. Current Czech regulation (Decree of the Ministry of Health No. 409/2005 Coll. on the hygiene requirements for products coming into direct contact with water and for water treatment) requires that these units should not decrease the hardness to more than 10%, or – if it is specifically designed to soften or partially de-mineralize water – it should keep minimum mineral levels in treated water as follows: TDS > 150 mg/L, Ca > 30 mg/L and Mg > 10 mg/L. Units not complying with this regulation should not be marketed. In practice this means that RO units without by-pass cannot be marketed as suitable for drinking water treatment as only re-mineralization cartridge cannot provide the required minimum. According to the NIPH experiences, based on analyses of water treated by dozens of RO units equipped with re-mineralization cartridge, the level of re-mineralization is absolutely insufficient from a health point of view as it can usually only provide less than 5 mg/L (Ca) or 2 mg/L (Mg).

The only possible use of RO units for home water treatment is in the situation that water (usually in private well) has high TDS and the by-pass in the RO unit is adjusted in the way that the treated water meets minimum Mg, Ca and TDS requirements. If water before treatment has already lower than minimum levels of Ca and Mg, it cannot be treated by RO. Since this regulation came into force, marketing of RO units for home water treatment without by-pass practically stopped and the number of people reporting health problems decreased substantially (Kozisek 2010, unpublished so far).

Some case studies of people with health problems after drinking osmotic water are included in the box.

In studies from Slovakia by Rapant et al. (2017b), the scientists suggested that the recommended levels of Ca and Mg in Slovakia should be increased from current Ca more than 30 mg/L and Mg 10–30 mg/L to Ca more than 89 mg/L and Mg 24–96 mg/L. The presented optimum range for Mg was 42–78 mg/L. Their study was based on ReI (relative mortality for cardiovascular diseases) data in relation to chemical composition of ground water in the Slovak Republic. The authors conclude: “Based on the achieved results, we recommend that the World Health Organization consider revising their definition of drinking water quality standards for Ca and Mg contents and water hardness.”

In the late 1970s, WHO commissioned a study to provide background information for issuing guidelines for desalinated water. The final report concluded; “not only does completely de-mineralized water (distillate) have unsatisfactory organoleptic properties, but it also has a definite adverse influence on the animal and human organism” (WHO 1980). In spite of the fact that this knowledge has been confirmed by a number of studies and any one did not impeach it, the approach of the WHO to the regulation of this area is very flabby, although the use of desalination increases continuously. Kozisek (2005) states that the four countries, Czech Republic, Hungary, Slovakia and Poland, that became part of the EU in 2004 included requirements of a minimum accepted hardness or levels of Ca and Mg in their respective regulations of drinking water. The awareness of the importance of minerals from drinking water is higher in these countries than in the Western parts of the EU, for historical reasons.

Some examples of boiling food in waters with different mineral contents are presented in the box.

Changes in the Mineral Content of Foods When Boiled in Waters of Different Hardness

Once an inverse relationship between water hardness and cardiovascular mortality was found and confirmed by a number of epidemiological studies in the 1960s and 1970s, some scientists began to suggest possible explanations or mechanisms of unexpectedly high magnitude of health effects in comparison with minor contribution of water to total daily intake of essential elements like calcium (Ca) and magnesium (Mg). For example, a systematic review of analytical studies investigating the association between cardiovascular disease and drinking water hardness (Catling et al. 2008) proved that 25% difference in mortality was caused by water Mg difference of only 10 mg/L (ca 5 vs. 15 mg/L). Considering daily water consumption of 2 L, it means the difference in Mg consumption is 20 mg/day, which represents only less than 10% of the recommended daily intake (280–350 mg for different populations).

One explanation is influence of water hardness on mineral content in food cooked in such water (potatoes, pasta, rice, some vegetables). If we cook these food items in soft water, there are higher losses of some essential elements into water, which is finally poured out. Consumers have in such situation not only lowered intake of nutrients (Ca, Mg) from soft water, but also from food. Unfortunately there have not been many studies looking into details and quantifying this effect.

The first benchmark experiments were done already in the early 1960s in the UK, where hard London water and very soft Glasgow water were used for cooking several sorts of vegetable and analysing cooking liquors for Ca (DSIR 1964). All the vegetables lost Ca to soft water and gained some Ca from hard

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water. However, the first regular experiment and its result were published by Dutch authors in 1981 (Haring and van Delft 1981). They cooked 4 food items (potato, cauliflower, carrot, and endive) in 6 different municipal tap waters of different hardness ranging from 0.6 mmol/L (Ca 17 mg/L; Mg 3.6 mg/L; conductivity 17 mS/m) to 3.6 mmol/L (Ca 114 mg/L; Mg 19 mg/L; conductivity 60 mS/m) and analysed mineral composition of the foodstuff. The most significant differences were found for Ca: the concentration of this element in potatoes and vegetables usually increased when cooking with hard-water types and decreased when soft water was used for cooking. Content of Mg in food decreased after cooking in any type of water, but losses were a little lower after cooking in hard water.

Similar types of experiments were conducted 25 years later at the National Institute of Public Health in Prague (unpublished results), using different foods (potatoes, pasta, beans, cabbage) and three municipal tap waters of various hardness: A) hardness 3.6 mmol/L (Ca 106 mg/L; Mg 13.5 mg/L; conductivity 42 mS/m), B) hardness 1.1 mmol/L (Ca 27 mg/L; Mg 3.5 mg/L; conductivity 15 mS/m), C) hardness 0.6 mmol/L (Ca 9 mg/L; Mg 3.7 mg/L; conductivity 13 mS/m). The results confirmed important impact of cooking on mineral composition of food and different behaviours of Ca and Mg. While losses were found in Mg (with the exception of pasta with 13% increase when cooked in hard water, and 7–8% decrease when cooked in soft waters), ranging from 25 to 50% with slight protective effect of hard water in the case of potatoes, more pronounced differences were found in the case of Ca. Its content in pasta and beans increased after cooking in all three waters, but six times higher in pasta in hard water than in soft water, and 2–3 times higher in beans in hard water. Ca content in potatoes increased after cooking in hard water by 83% (in comparison with raw potatoes), but after cooking in soft waters both slight increase (by 18%) and decrease (by 10%) was found. Ca content in cabbage did not change significantly after cooking, it differed by minus 7% to plus 3% (hard water) in comparison with raw cabbage (Kozisek, personal communication).

Thus the results show the real impact of water hardness on mineral composition of vegetable and other foodstuff cooked in the water.

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Chapter 8
The Positive Effects of Drinking Water on Mineral Balance; Optimum Nutrient Ratios and Protection Against Toxic Elements by Nutrient Elements

Ingegerd Rosborg

Abstract Mineral ratios are important because minerals can operate both antagonistically and synergistically with each other. Ca and Mg are synergists, but elevated Ca:Mg ratio in especially mineral-poor water will increase the risk of acute myocardial infarction due to suppressed Mg absorbtion. High concentrations of Mg and Ca in water may be protective against elevated levels of Fe, Pb, U and Cd, since especially Ca acts antagonistically against Pb, Cd and U, and Mg against Fe. The risk of rectal cancer from THMs is increased when Mg is low. The ratio (Ca + Mg + K):Al was higher in alkaline waters and women's hair than in acid, and women consuming alkaline well waters were healthier. In addition, the risk of getting cancer from elevated tetrachloroethylene (PCE), trichloroethylene (TCE), and trihalomethanes (THM) may be lower than the risk for cardiovascular diseases, due to low levels of Ca, Mg and HCO_3 in drinking water.

Absorption and utilization of minerals from drinking water is determined by several factors. Thus, a number of elements are synergists and/or antagonists; for example Se-I and Cu-Fe are pairwise dependent upon each other for absorbtion or metabolism. Minerals that share transporters can be mutually inhibitory; Ca-Zn, Ca-Pb, Cd-Zn, and Zn-Cu (WHO 2005). Selenium is somewhat less absorbed from water than from food containing Se-amino acids, while most minerals are more easily absorbed from water, since they are in ionic form in water. The bioavailability of Ca, Fe, Mg, P, Cu or Zn is depressed by foods/diets high in phytate, such as cereals. Phosphorus and triglycerides bind to Ca, and may reduce its absorption. Cu and Zn are less absorbed in elderly people, and Fe, Zn, Cu, Mn and Cr are absorbed to a higher extent in deficiency. Sulphides can bind Cu, and other heavy metals (WHO

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2005), and Ca is more readily absorbed in an acid surrounding in the intestines (Wynn et al. 2009; Burckhardt 2008). Oxalates and high Fe intake decreases Cr bioavailability (WHO 1996). Elevated Zn, Fe and Mo decrease Cu bioavailability (WHO 1996). Studies on mice have shown that F improves Fe absorption or use (Bowman and Russell 2006). High Ca intake decreases Mn bioavailability (WHO 1996). Alterations in Fe status may occur from intake of drinking water with elevated Mn concentration (FNB 2001). Si controls the metabolism of Ca and Mg, and acts antagonistically against Al (Schwarz et al. 1977). Aluminium interacts with Ca, F, Fe, Mg, P and Sr, and is used to treat fluorosis and to reduce PO_4 absorption in uremic patients (WHO 1996). Ca in water may act protectively against uptake or distribution of elements like Pb and Cd (WHO 2005), and Cd binds to an enzyme, metallothionine, which normally contains Zn or Cu (WHO 1996). Selenium provides protection from Hg and methyl mercury toxicity (Goyer 1995). Mg and Ca may be used to decrease the negative effects of too much Fe from water (Banner and Tong 1986). Ca and Mg are synergistic, but elevated Ca:Mg ratio in water and thus deficiency of Mg in the diet and in water may significantly increase the risk of acute myocardial infarction (AMI), and coronary heart diseases are connected to soft drinking water with high Ca:Mg ratio (Kousa et al. 2006). Amounts of Sn similar to those found in human diets can depress Zn, Mn and Cu status (Bowman and Russell 2006; Pekelharing et al. 1994). Minerals in drinking water may even influence substances such as THMs (trihalomethanes), as the risk of rectal cancer from THMs was increased when the Mg level was low in drinking water (Kuo et al. 2010).

In a Swedish study on acid and alkaline well waters, the ratio (Ca + Mg + K):Al, was significantly higher in alkaline waters, average 1412, compared to average 239 in acid well waters, indicating protection against the toxic metal Al in alkaline waters. In the hair of women, the ratios varied in a similar way, and were 804 and 177 on average, respectively. Women consuming alkaline well waters were healthier (Rosborg 2005; Rosborg et al. 2002, 2003).

In a Swedish study on bottled waters, some mineral ratios were extreme. The median Na:K ratio in the total material was 5.4:1, but five brands showed elevated Na:K ratios, 54–100:1. Some of those were supplemented with Na salts. The Ca:Na ratio of these brands was 0.03:1, while the median ratio was 1.4:1. Fifteen waters had Ca:Na ratios below 1:1, and six below 0.1:1, indicating very soft waters, poor in especially Ca, but they also had extremely low concentrations of Mg. The median ratio of Ca:Mg in the bottled waters was 4.7:1. In three brands the ratio exceeded 20:1, indicating very hard and Ca-rich waters (Rosborg et al. 2005). The influence of drinking water with no minerals and the influence of different mineral ratios need to be studied further.

The above-mentioned antagonistic and synergistic relations between elements are summarized in Table 8.1. Among nutrient elements, two of them may be synergistic at low concentrations, but at elevated concentrations or improper ratios they can be antagonists. This accounts for elements such as Ca and Mg.

Chemical substances are regulated in the EU, WHO, etc. and water suppliers need to take actions and follow them. However, such actions may result in an even more health-threatening water. This is reflected in the box.

Table 8.1 Some examples of antagonism and synergism among elements found in drinking water

Antagonists (nutrient-toxic element)	Antagonists (nutrients)	Synergists (nutrients)
Ca-Cd	Ca-Co	Ca-Mg
Ca-Pb	Ca-Fe	Cu-Fe
Ca-U	Ca-Mg (high levels or improper ratios)	Cu-Zn
Cu-Zn	Ca-Mn	F-Fe
Se-Hg	Ca-Zn	Se-I
Si-Al	Cu-Cd	
Zn-Cd	Cu-Mo	
Al-F (if too high F level)	Cu-Zn	
	Fe-Cr	
	Fe-Cu	
	Fe-Mn	
	Mg-Fe	
	Zn-Cu	

Balancing Two Different Chemical Risks

Current regulatory schemes for drinking water safety cover a list of most common chemical pollutants, mostly based on historical experience (nitrates, lead, arsenic, etc.), but partially also on knowledge on emerging contaminants. A number of these chemical substances – in concentration found in drinking water – has only hypothetical or negligible health risks; nevertheless, due to regulation, water producers are forced to manage every, even slight non-compliance, with established limits. Management options include installation of new water treatment technology, selection of new source of water or mixing water from polluted and unpolluted sources. As most of such regulatory schemes ignore parameters which have much higher health risk and population impact if present in water in too low a level (magnesium, bicarbonates, calcium), accepted remedial options may in fact represent much higher population risk if these aspects are not taken into account. Typical example is removing some element by reverse osmosis, which at the same time substantially reduces the level of essential and health supporting minerals in drinking water. Another example of balancing two different chemical risks may be illustrated with results from the study done by the Czech National Institute of Public Health (NIPH) for one Czech municipality.

Czech town X. of 10,000 population uses local groundwater sources polluted by both tetrachloroethene (PCE) and trichloroethene (TCE). Water is treated by aeration (stripping) and concentration of sum TCE + PCE in finished water is about the limit value 10 μg/l. The health risk from this level of pollution in this town is about 1 case of cancer per 25 years. The operator

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considered two options for improvement: either to renew and intensify treatment of local water or to connect with adjacent water supply with unpolluted groundwater. However, local groundwater has magnesium level about 30 mg/l, but adjacent water supply only 5–8 mg/l. For this reason, the operator turned to the NIPH to calculate health risks from both options to have a scientific ground for proper decision-making.

If the town switches to adjacent source with much lower Mg content for consumers it would represent about 20–30% higher risk of death from cardiovascular diseases (Catling et al. 2008). If we take into account high incidence of cardiovascular diseases in the European population, the change of water source may lead to several deaths per year – in comparison with the "benefit" of preventing 1 case of cancer per 25 years. The operator decided not to switch the source, but continue to treat local water to avoid substantial increase of health risk for consumers (Kozisek 2018, unpublished).

A similar situation was when total softening was performed in water with 15 μg/L of uranium (U) in a community in the Stockholm archipelago. The softening totally eliminated the Ca, which is an antagonist against U, making the water more toxic. Such facts need to be considered in future drinking water regulations.

Desired Ca/Mg ratio is 2–3:1, and Na/K 2–5:1. However, the Na/K ratio regularly is much larger especially if there is salt intrusion into the water source or softening, with NaCl, is performed, increasing the Na concentration. In addition, K in water generally does not exceed 10 mg/L or even 5 mg/L, while Na often is higher than 50 mg/L. Only water sources from dolomite limestone and, e.g. special shales give water high Mg levels, while the Ca/Mg ratio seldom is as low as 2–3:1.

Thus, high nutrient mineral concentrations in the drinking water, as well as mineral balance, is important:

- Since minerals in water are in ionic form and generally more readily absorbed than from food, where the minerals are found to, e.g., proteins, and first need to be peeled
- To avoid corrosion of pipes and other material in contact with the water – Ca salts in the water can form a covering shield on the pipe surface, hindering further dissolution of especially Cu or Pb from pipes
- To increase the uptake of minerals in the intestines, since nutrient and toxic elements may use the same channels to get into the body, and there may be a competition between them
- To enhance their action inside the body, as essential minerals may use the same transporters, and there may be a competition, such as between Ca and Pb
- To enhance their action inside the body, such as Ca vs Pb, both of which form stable phosphates in bones, but only Ca builds appropriate bone material

- As high concentrations of especially Ca and Mg are protective against e.g. cardiovascular diseases and decreasing the levels of those elements while eliminating a toxic substance may be even more harmful than preserving the toxic substance and the mineral content at the original level

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Chapter 9
Drinking Water Regulations Today and a View for the Future

Ingegerd Rosborg and Frantisek Kozisek

Abstract Present drinking water regulations include highest accepted levels of toxic metals and organic pollutants, harmful bacteria, etc., as well as the highest accepted levels of water agents, e.g. Fe, Mn, Cl or Ca, which may cause precipitation, high turbidity or discolouring. However, water with some minimal levels of Ca, Mg or HCO_3 is protective against cardiovascular diseases, which is the biggest killer of people around the world, as well as osteoporosis and depressed cognitive function in the elderly, and probably also diabetes mellitus, etc. and should not be decreased in case they are not present in some very excessive levels. In addition, microelements like Se, Mo or I, appearing mostly in alkaline (hard) waters, are beneficial in preventing specific diseases. Other natural elements like Cl or SO_4 contribute positively to water taste and osmolality. Thus, future regulations should include lowest acceptable concentrations or recommended ranges of a number of elements, as well as element ratios. Especially the lowest acceptable concentrations of Ca, Mg and HCO_3 where we have the best evidence of protective health effects should be set to prevent unnecessary removal of them from drinking water.

9.1 Present Regulations and Their Shortcomings

In 1958, the World Health Organization (WHO) published “International Standards for Drinking water” and in 1984 “Guidelines for Drinking water Quality”, which was subsequently revised. In 2011, the fourth edition of WHO guidelines was published with the first addendum in 2017. Drinking water regulations have so far been focused on water free of acutely toxic organic pollutants, bacteria and toxic elements.

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The inorganic toxic elements that are regulated are Al, As, Cd, Cu, Pb, Hg, NO_3, Cr, NO_3 and U. From a practical point of view there are also regulations in municipal waters to prevent too high Fe, Mn or Ca content, as they may cause precipitation in pipes and on sanitary equipment, discolouring of clothes (Fe, Mn) and unacceptable taste of water (WHO 2011; EU 1998). Thus, regulations only include upper limits for toxicological, aesthetic or other reasons. No attention is paid to the need of minerals in drinking water for a good health or avoiding the burden of disease.

Due to the process of revision, the European Commission (EC) revealed the proposal of new Drinking Water Directive on the 1 February 2018 (EC 2018), which was at the time of writing the second edition of this book (early spring 2019) after discussions in the Council and the European Parliament (EP). The original proposal included some more toxic elements as parameters (e.g. U), but at the same time suggested to remove all indicators (current Annex I, Part C). On the other hand, it requested water suppliers to inform consumers about water quality in a broad range of minerals: iron, manganese, borate, chloride, fluoride, hydrogen carbonate, phosphate, silicate, sulphate, sulphide, aluminium, ammonium, calcium, magnesium, potassium and sodium. However, no minimum or desirable ranges are suggested and so no guidance for consumers is provided. The final version cannot be foreseen before the deadline for this edition, but it seems that the aspect of beneficial nutrients is either omitted again or treated only generally. The EU Council recommended to keep all indicators and proposed to introduce provision, that water which is softened or demineralized should keep some minimum amount of beneficial minerals like Ca and Mg and that the EU member states should reflect it in their national regulations. The final negotiation between the EC, EP and Council started in October 2019.

The WHO and EU drinking water standards are presented in Table 9.1.

For WHO Guidelines for drinking water Quality, see further:

http://apps.who.int/iris/bitstream/handle/10665/254637/9789241549950-eng.pdf;jsessionid=5EB265797155E30B049A07C4087B29C5?sequence=1

For EU Council Directive 98/83/EC, see further:

https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31998L0083&from=EN3/

9.2 Suggestions for Future Drinking Water Regulations and the Need for Declaration of Mineral Content/Mineral Balance in Different Types of Drinking Water

As described above, in the last few decades a lot of new knowledge has been developed regarding health aspects of major inorganic minerals and ions in drinking water, which should be highlighted for regulatory authorities and the public at large.

Table 9.1 The WHO and EU drinking water standards (WHO 2011; EU 1998)

Parameter		WHO Guideline value	EU Parametric value	Unit
pH			6.5–9.5	
Antimony	Sb	0.02	0.005	mg/L
Aluminium	Al	0.9 n.e.	0.2	mg/L
Ammonium	NH_4	n.e.	0.50	mg/L
Arsenic	As	0.01	0.01	mg/L
Boron	B	2.4	1.0	mg/L
Barium	Ba	0.7	n.e.	mg/L
Beryllium	Be	0.012 n.e.	n.e.	mg/L
Bromate	BrO_3	0.01	0.01	mg/L
Cadmium	Cd	0.003	0.005	mg/L
Chloride	Cl	250 (taste, no health based g.v.)	250	mg/L
Chromium	Cr	0.05	0.05	mg/L
Conductivity			2500 (20 °C)	μS/cm
Copper	Cu	2	2.0	mg/L
Cyanide	CN	0.5 n.e.	0.05	mg/L
Fluoride	F	1.5	1.5	mg/L
Iodine/iodide	I	n.e.	n.e.	mg/L
Iron	Fe	0.3 (taste and appearance, no health based g.v.)	0.2	mg/L
Lead	Pb	0.01	0.01	mg/L
Manganese	Mn	0.4	0.05	mg/L
Mercury	Hg	0.006	0.001	mg/L
Molybdenum	Mo	0.07	n.e.	mg/L
Nickel	Ni	0.07	0.02	mg/L
Nitrate	NO_3	50	50	mg/L
Nitrite	NO_2	3	0.5	mg/L
Phosphate	PO_4	n.e.	n.e.	mg/L
Rubidium	Rb	n.e.	n.e.	mg/L
Selenium	Se	0.04	0.01	mg/L
Sodium	Na	200 (taste, no health based g.v.)	200	mg/L
Sulphate	SO_4	250 (intest. disturb, no health based g.v.), corrosion	250	mg/L
THM		The sum of the concentration divided by the guideline value for the different THMs present should not exceed 1	0.1	mg/L
Uranium	U	0.03	n.e.	mg/L
Zinc	Zn	3(aesthetic, no health based g.v.)	n.e.	mg/L
Radioactivity		0.1 mSv/year	0.10 mSv/year	

The overall aim is to induce people to drink more healthy water that contains beneficial minerals and ions. Thus, the need now is for new regulations for minimum and maximum limits of beneficial minerals in drinking water in view of the mounting scientific evidence of the major benefits possible by drinking water with optimum levels of minerals, particularly Ca, Mg and HCO_3. Since such water has been shown to be directly beneficial for reducing especially cardiovascular mortality, the biggest killer of people around the world, it is required to introduce appropriate regulations (Altura and Altura 2009). Such water generally also contains other nutrient minerals, protective against cardiovascular and other diseases, such as Se, Mo and SO_4.

Since the 1960s, some authors consider the absolute content of Ca and Mg in water (diet) to be of the same importance as the Ca:Mg ratio (Seelig 1964; Karppanen 1981; Durlach et al. 1989). Durlach's recommendation (1989) that the Ca:Mg total intake ratio be 2:1 as required for the best Mg absorption is still valid. Increase in Ca:Mg ratio was associated with increasing risk for premature mortality from IHD and AMI (Rubenowitz et al. 1999; Durlach et al. 1989) while the decrease in the Ca:Mg ratio was apparently associated with an increasing risk for gastric cancer (Sakamoto et al. 1997). A risk-reducing suggested Ca:Mg ratio may well be 2–3:1. The Na:K ratio in drinking water is in general around 10:1 (Aastrup et al. 1995), since K is generally very low in drinking water, and this is why drinking water is not considered to be as source of K (WHO 2011). The recommended ratio might be 2–5:1. In Swedish groundwaters the ratio of Ca:Na and Na:K is in the range of 1–10 (SNV 1999).

Ion balance is used to check analytical results. Total anions must be in balance with total cations. Therefore, the sum of the concentrations of anions should equal the total concentration of cations and the ratio of total anions to total cations should be 1. Anion-cation balances based on the ions Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, SO_4^{2-}, Cl^-, HCO_3^- and CO_3^{2-} (in milli-equivalents per litre) for over 1500 analyses of natural waters have been examined. While most waters showed an ion balance with a ratio within 1 ± 0.10 for the cations Na^+, K^+, Ca^{2+}, Mg^{2+}, and anions SO_4^{2-}, Cl^-, HCO_3^- and CO_3^{2-} of the total of these ions, there was a lack of ion balance associated with acidic waters and waters with low ionic concentrations. Waters which were alkaline, which contained soluble silica generally showed an excess of anions (Johnson et al. 1979).

On the basis of citated scientific studies in this monograph, safe and beneficial optimum ranges are suggested. The aim with these ranges is to provide water suppliers and producers a health-based reference to relate to for their specific water and its mineral content and mineral balance when presenting it to the public. In addition, the aim is to provide guidance for water producers to make provision for desirable water quality and fit in these ranges as much as possible in water production when water source, filters or other processes are chosen.

In Tables 9.2, 9.3, 9.4 and 9.5, our suggested safe ranges for a number of nutrient macro-minerals and ions, as well as ratios between minerals, are presented.

Table 9.2 Suggested desirable ranges for some macro-elements and ions in drinking water from a health point of view

Parameter	Range	Unit
pH	7.0–8.5	
Hardness	8.0–14.0	°dH
	(1.4–2.5)	(mmol/L)
Calcium (Ca)	30–80	mg/L
Magnesium (Mg)	10–50	mg/L
Bicarbonate (HCO_3)	100–300	mg/l
Potassium (K)	10–30	mg/L
Sodium (Na)	20–70	mg/L
Sulphate (SO_4)	25–100	mg/L
Total Dissolved Solids (TDS)	100–500	mg/L

Table 9.3 Suggested desirable ranges for some micro-elements in drinking water from a health point of view

Parameter	Range	Unit
Boron (B)	0.1–1	mg/L
Chloride (Cl)	20–50	mg/L
Chromium (Cr III)	0.01–0.05 (CrVI kept as low as possible)	mg/L
Cobalt (Co)	0.005–0.02	mg/L
Copper (Cu)	0.02–0.2	mg/L
Fluoride (f)	0.5–1.0	mg/L
Iodine (I)	0.005–0.05	mg/L
Iron (Fe)	0.02–0.2	mg/L
Lithium (Li)	0.01–0.1	mg/L
Manganese (Mn)	0.005–0.025	mg/L
Molybdenum (Mo)	0.005–0.05	mg/L
Phosphate (PO_4)	0.02–0.1	mg/L
Rubidium (Rb)	0.01–0.1	mg/L
Selenium (Se)	0.005–0.03	mg/L
Silicon (Si)	2–10	mg/L
Vanadium (V)	0.001–0.01	mg/L
Zinc (Zn)	0.02–0.2	mg/L

9.3 Bottled Waters

Bottled water label can be chosen from time to time and is generally not consumed every day or just a couple of glasses per day, while suggested ranges can be larger. In addition, some very hard waters with elevated mineral levels can be very important for people suffering from, e.g., osteoporosis and cancer, which are connected to

Table 9.4 Suggested safe upper limits for some potentially toxic and ions in drinking water from a health point of view

Parameter	Range	Unit
Aluminium (Al)	<0.2	mg/L
Ammonium (NH_4)	<0.5	mg/L
Antimony (Sb)	<0.005	mg/L
Arsenic (As)	<0.01 (0.001–0.01)	mg/L
Barium (Ba)	<1 (0.01–0.1)	mg/L
Beryllium (Be)	<0.005	mg/L
Bismuth (Bi)	<0.001	mg/L
Bromate (BrO_3)	<0.01	mg/L
Cadmium (Cd)	<0.003	mg/L
Cyanide (CN)	<0.05	mg/L
Lead (Pb)	<0.005	mg/L
Mercury (Hg)	<0.001	mg/L
Nickel (Ni)	<0.05 (0.01–0.05)	mg/L
Nitrate (NO_3)	<50	mg/L
Nitrite (NO_2)	<0.5	mg/L
Radioactivity	<0.1	mSv/Year
Silver (Ag)	<0.01 (0.001–0.01)	mg/L
Strontium (Sr)	0.2 (0.02–0.2)	mg/L
THM (TriHaloMethanes)	<0.015	mg/L
Tin (Sn)	<0.1 (0.01–0.1)	mg/L
Titanium (Ti)	Not set	mg/L
Uranium (U)	<0.015	mg/L

Table 9.5 Suggested desirable ranges for some mineral ratios in tap water from a health point of view

Ratio or other	Safe range	
Ca:Mg	2–3:1	
($Mg + SO_4$)	100–400	Mg < 150 mg/L
($Ca + Mg + Na + K$) = ($SO_4 + CO_3 + HCO_3 + Cl$)	Ion balance	meq/L

acidic tissues, can be regarded medical waters and be used for a shorter time or a couple of glasses each day. These will give a substantial contribution to the daily intake of especially Ca and Mg, but also the pH-regulating HCO3 (Table 9.6).

9.4 Advice to Drinking Water Producers and Suppliers

The following points form a potentially good practical guide for producers and suppliers of drinking water.

Table 9.6 Suggested desirable ranges for some mineral ratios in bottled water from health point of view

Parameter	Range	Unit
pH	7.0–8.5 (non-carbonated)	
pH	4–8.5 (carbonated)	
Hardness	8.0–20.0 (1.4–2.5 mmol/L)	°dH
Calcium (Ca)	30–250	mg/L
Magnesium (Mg)	10–75	mg/L
Bicarbonate (HCO_3)	100–350	mg/l
Potassium (K)	10–30	mg/L
Sodium (Na)	20–100	mg/L
Sulphate (SO_4)	25–350	mg/L
Total Dissolved Solids (TDS)	100–700	mg/L

1. Standards must be followed to remain within the law.
2. Any water, public "tap" or bottled, should have a declaration regarding its mineral content, extensive analyses presented. Declarations should be readily available for the public and compared to the suggested ranges in this monograph.
3. RO-treated water should be re-mineralized before distribution to the public to at least the lowest concentrations in the suggested intervals for at least Ca, Mg, HCO_3 and SO_4, or blended with raw waters to maintain its mineral ratios. Macro- and micro-mineral content, as well as mineral balance should be considered, and the water should be free from toxic metals and substances. Results from extensive analyses should be presented and compared to the ranges. This includes RO-treated bottled waters (although current EU and WHO regulatory framework does not support this approach).
4. Water softening filters should preferably not reduce the hardness to levels of <8–10°dH, or Ca <50 mg/L and Mg <10 mg/L, absolute minimum 6°dH. Extensive analyses are presented and compared with the suggested ranges.
5. Alkaline filters used to increase pH for corrosion purposes should not be performed by adding NaOH, since only Na and the alkalinity (only slightly) is raised. Dolomite limestone, mixture of dolomite and calcite limestone or other rock free from toxic substances and in good mineral balance should be used.
6. In water with one or more toxic metals, concentrations of the protective (antagonistic) elements should be as close to the upper limit of the suggested intervals as possible. RO or similar treatment method should not be performed to decrease levels of toxic substances, due to the risk of elimination of antagonist; Ca and/or Mg will be, and especially not if the water has low hardness, in the lower part of the range.

Elements and ions are presented without charges in this monograph, and in general only with their chemical letters. Elements and ions are presented in Table 9.7.

Table 9.7 Mineral elements and ions in drinking water, as presented in the text, and their chemical formulae

Element	In the text	Ion(s) in water
Aluminium	Al	Al^{3+}
Ammonium	NH_4	NH_4^+
Antimony	Sb	$Sb(OH)_6^-$, antimonate
Arsenic	As	As (V): AsO_4^{3-}(arsenate)
Barium	Ba	Ba^{2+}
Beryllium	Be	Be^{2+}
Bicarbonate	HCO3	HCO_3^-
Boron	B	$B_4O_7^{2-}$, borate
Bromate	BrO3	BrO_3^-
Cadmium	Cd	Cd^{2+}
Calcium	Ca	Ca^{2+}
Chloride	Cl	Cl^-
Chromium	Cr	Cr^{3+}
Cobalt	Co	Co^{2+}
Copper	Cu	Cu^{2+}
Cyanide	CN	CN^-
Fluoride	F	F^-
Iodine	I	I^-
Iron	Fe	Fe^{2+}, Fe^{3+}
Lead	Pb	Pb^{2+}
Lithium	Li	Li^+
Magnesium	Mg	Mg^{2+}
Mangenese	Mn	Mn^{2+}
Mercury	Hg	Hg^{2+}
Molybdenum	Mo	MoO_4^{2-} (molybdate)
Nickel	Ni	Ni^{2+}
Nickel	Ni	Ni^{2+}
Nitrate	NO_3	NO_3^-
Nitrite	NO_2	NO_2^-
Phosphate	PO_4	PO_4^{3-}
Potassium	K	K^+
Rubidium	Rb	Rb^+
Selenium	Se	SeO_4^{2-} (selenate)
Silicon	Si	SiO_4^{2-} (silicate)
Silver	Ag	Ag^+
Sodium	Na	Na^+
Strontium	Sr	Sr^{2+}
Sulphate	SO_4	SO_4^{2-}
Tin	Sn	Sn^{2+}
Titanium	Ti	Ti^{4+}
Uranium	U	U^{3+}, U^{4+}
Vanadium	V	VO_4^{3-}, $V_2O_7^-$ (vanadate)
Zinc	Zn	Zn^{2+}

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