
Natural groundwater quality and health

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ABSTRACT

Natural groundwater composition and quality is of concern because it is used worldwide as a freshwater supply. Discarding artificial pollution, epidemiological studies have shown that many communities suffer important diseases linked to the groundwater ingested since several tens of years ago. As the available resources of freshwater decrease due to pollution and overexploitation, and the need of water increases, more efforts have to be devoted to guarantee water quality. Of course preventing pollution is the main task but studying and controlling the natural groundwater quality is also very important, mainly in developing countries. To study the relationship between natural groundwater composition and health implies working in many scientific disciplines such as hydrology, geology, geochemistry and toxicology. During its cycle, water acquires its natural composition depending on the hydrogeological scenario, which, in turn, depends on the climate, topography and rock properties (hydraulic properties, chemical composition). Nearly all natural waters contain traces of most chemical elements but often at extremely low concentrations. Major species invariably make up over 99% of the solute content. Major compounds as well as trace elements can be essential, toxic, potentially toxic and potentially beneficial. Special attention has to be paid to chemical elements present in many natural waters whose insufficient or excess intake produces critical illness and whose intake is mainly through the ingestion of water. A first approach to groundwater quality can be made using element concentrations in water but many efforts have to be devoted to perform epidemiological and risk assessment studies based on intake doses of chemical species.

KEYWORDS | Groundwater quality. Health. Natural composition. Essential elements. Toxic elements.

INTRODUCTION

Scope

Water quality and health

Water is the main renewable constituent of the human body (70-80% of weight) and therefore it is crucial for the health and the welfare of the human being. It is important

to distinguish between the two main uses of water related to health: ingestion and social uses. Concerning ingestion, water is the main drink (or major constituent of elaborated beverages) and an important constituent of many foods. Moreover, water is used during the preparation of many cooked dishes.

By social use we mean the use of water as an essential element for the body hygiene and environmental quality.

During this use water is not directly ingested but it gets in touch with the skin, mouth, eyes and its vapour and aerosol can be inhaled. Water also plays a primordial role in the sanitation of the houses and communities. This later aspect referring to the sanitation and environmental quality will not be explicitly studied in this work.

Health of the individuals and the communities is strongly related to the availability of a sufficient amount of quality-guaranteed water. However, the minimum amount of water needed per inhabitant and its minimal quality are relative concepts. The difficulty of establishing universal guidelines for drinking water quality arises from the task of linking the concentration of a given chemical and its health effect. The latter depends on the properties of the element and the intake dose, which, in turn, depends on the concentration in water, among other factors.

Natural groundwater

Groundwater originates from the deep infiltration of rain and surface water. In general terms groundwater flows slowly through geologic formations and remains in contact with minerals often isolated from the atmosphere. Because of the partial isolation with respect to the surface of the Earth and the long residence time in aquifers, groundwater has a much higher inertia than surface waters both in terms of renovation of resources (quantity) and vulnerability to pollutants (quality).

Both surface and groundwater are used by humans as water supply. The present paper will only deal with the groundwater natural composition. This excludes any polluted groundwater as well as groundwater coming from an artificial recharge or well injection.

Nowadays it is becoming more difficult to discriminate between natural composition and polluted water. There is no standard for defining natural water. Many efforts are being devoted to define the reference natural groundwater quality in Europe (Instituto Geológico Minero de España -IGME-, 2002).

Objectives and methodology

The objective of this paper is to review why and how natural groundwater affects human health. We will focus on the chemical elements that are important because either they are essential or can be toxic when ingested in inappropriate doses. Other reference works are devoted to review the natural groundwater composition but without linking it to the human health (Hem, 1985). Hydrothermal waters are considered because they are natural and related with human health.

Despite the fact that the paper is focused on natural groundwater quality and health, most of the information referring to the chemical elements, like their behaviour in the environment or their toxic effects, is valid for any origin of the elements and most of the ingestion paths. The potentially toxic and/or essential natural elements will be studied with special emphasis. A review of the general aspects concerning the water cycle and the natural groundwater composition, the health effects and the hydrogeological scenarios will be made.

The main section of the paper will be devoted to describe the main chemical elements naturally occurring in groundwater and of concern because they are essential and/or potentially toxic. The therapeutic use of groundwater will also be included.

General aspects

Hydrogeological scenarios

Natural chemical composition of groundwater results from two main processes: the concentration by evaporation of the atmospheric salts coming from marine aerosols, dust and dissolved salts in rainwater; and the water interaction with ground minerals and substances (Llamas et al., 2001).

The resulting groundwater concentration depends on a wide set of processes and not only on the mineral composition of the aquifer rocks. The general hydrogeologic framework of the area also influences groundwater quality. Therefore, it is more appropriate to talk about hydrogeological scenarios or environments than geological formations.

A hydrogeological environment is a conceptual model of morphological, geological and climatic parameters that determine the main groundwater flow features in a given area (Tóth, 1970). Three components of the hydrogeological environment control the parameters of the groundwater flow regime: topography, geology and climate. Such components are in turn formed by several parameters. The size, shape, orientation and abundance of topographic elements form topography. Geology refers to the soluble material contents, configuration of heterogeneities (stratification, lenses, fracturation, karstification, anisotropy). Climate includes temperature, rainfall and potential evapotranspiration.

Climatic factors control the available amount of water in a given system or scenario. Topography gives the limits of the system as well as the driving energy for the groundwater flow. Geology sets the flow paths within the system and the geochemistry of water (Tóth, 2000).

Most of the water types can be found in many geological formations, depending on the climate and the hydrogeological situation. The primary present rocks give the elements potentially present in groundwater. But, those elements will be actually present in groundwater only if the hydrogeochemical conditions allow it. Residence time and oxidation state of the medium are probably the main factors that control the final groundwater composition, besides the host rock composition.

Typically, the TDS (Total Dissolved Solids) of groundwater increases along the flowpath, the dominant anion goes from bicarbonate to sulphate and finally chloride, the oxygen and CO₂ contents decrease, the redox potential becomes negative and the pH increases. Hence, in the recharge areas mineral dissolution takes place while in the discharge areas there is precipitation (mainly of salts) (Tóth, 2000).

A general relationship between the mineral composition of a natural water and that of the solid minerals with which the water has been in contact is certainly to be expected. This relationship must be comparatively simple as in the case of an aquifer that receives direct recharge by rainfall and from which water is discharged without contacting any other aquifer or water. Or the situation may be rendered complex by the influence of one or more interconnected aquifers of different composition, the mixing of different water, chemical reactions and biological influences. Processes involved in soil formation and the soil composition of the area may have considerable influence on composition of underground water (Hem, 1985).

Most rocks are complex mixtures of minerals that differ widely in their solubility in water. Most rocks, except the evaporites, are made of minerals that are not readily soluble. The more soluble components will exert a major influence on the composition of water circulating through the rock. Often, minor components may control major features of the groundwater composition.

Geochemistry

The chemical composition of groundwater is the combined result of the composition of water that enters the groundwater reservoir and reactions with minerals present in the rock that may modify the water composition. The number of possible chemical reactions that may occur in a groundwater reservoir is tremendous and the interpretation of observed water quality differences is difficult (Appelo and Postma, 1993).

Rainwater is the main source of groundwater. The composition of rainwater is determined by the source of the water vapour and by the ions that are acquired by water during transport through the atmosphere. Near the

coast rainwater strongly resembles diluted seawater. As the distance from the coast increases, the concentration of ions that are directly derived from seawater decreases. Marine aerosols, continental dust and evaporation processes lead to the final compositions of the rainwater. Rainwater that infiltrates acquires solutes through interactions with soil and rocks. Most of terrestrial water has less than 1000 mg/l of total dissolved solids (TDS).

At the watershed scale the most important natural processes affecting the groundwater chemistry are evaporation and evapotranspiration, selective uptake of ions by vegetation, decay of organic matter (oxidation/reduction), cation exchange, dissolution of minerals, precipitation of secondary minerals and mixing of water (Appelo and Postma, 1993). Nearly all natural waters contain traces of most chemical elements but often at extremely low or unquantifiable concentrations. Nine major species (HCO₃⁻, Na⁺, Ca²⁺, SO₄²⁺, Cl⁻, NO₃⁻, Mg²⁺, K⁻ and Si) invariably make up over 99% of the solute content in natural waters (Edmunds and Smedley, 1996). The relative abundance of minor and trace elements can change significantly depending on geochemical conditions.

Depending on the physical and chemical conditions, the dissolved elements in water are present under specific chemical forms (free, hydrated, aqueous complexes, sorbed or precipitated). The speciation of chemical elements affects its distribution, mobility (advection, dispersion, diffusion, solid transport, and immobilisation) and toxicity (Plant et al., 1996; Stumm and Morgan, 1996). Some of the most important controls, particularly on trace element speciation and mobility, include pH, redox potential (Eh), temperature, surface properties of solids, the abundance and speciation of potential ligands, major cations and anions, the presence or absence of dissolved and/or particulate organic matter, and (micro)biological activity (Plant et al., 1996).

Two of the most important factors directly controlling mobility and solubility are Eh and pH. The aqueous chemistry of an element is affected profoundly by changes in oxidation state (Smedley and Edmunds, 2002), while dissolution reactions, including hydrolysis, inorganic complexation and sorption, are more controlled by pH. In general, under conditions of high pH anions and oxyanions are more mobile and most cations are less mobile, while at low pH this tendency reverses.

Toxicology and risk

All the major compounds of water and many of minor and trace elements are essential for metabolism and human health.

The intake of chemical elements by humans is made mainly by ingestion of solids (food and soil) and

liquids (food, drinks and water) but also breathing (air and aerosols) and dermal contact (water and soil). Epidemiology relates the incidence and geographic distribution of diseases to probable causal factors such as the accumulation of excess amounts of toxic elements (separating or not the different exposure paths) or the absence of necessary elements in an organism (Siegel, 2002).

Drinking water is an important path of essential element intake but not the only one; for some elements is not even the most important. Element speciation in the environment and in the human digestive system also controls the dose, the uptake, and therefore, the toxicity. The toxicity of an element can change substantially from one species to another one. For this reason, the epidemiological studies often refer to specific species present and not to the total amount of the element. In addition, the toxicity of some elements is not due to themselves but to the effect they have on the intake or accumulation of other essential and/or potentially toxic elements.

The effect of toxic elements on humans can or can not be carcinogenic. While carcinogens are evaluated with the chronic dose intake (they are bioaccumulative), the non-carcinogens are evaluated with the acute doses (short ingestion episodes because the elements do not accumulate, even if the effects can accumulate). Risk analysis studies must be based on the doses and not on the concentrations because it can be more dangerous to reside long time in a place with slightly bad quality groundwater for a given element than to ingest sporadically worse quality groundwater.

Therefore, it is complicated to establish universal quality criteria, guidelines and recommendations for drinking water. The groundwater quality is measured based on the concentrations of the dissolved chemical elements (or chemical species in the best case), and not on its use and the associated risk. Nevertheless, the habits of home use of water are quite well known and they are very homogeneous inside each social group, although those habits are quite different between areas with important geographic or social differences.

The experimental data usually needed to relate concentrations with doses (minimal or maximal) and with the undesirable effects over the health (carcinogens or not carcinogens) are not always available, although they are becoming more so. Nevertheless, at this moment, the most rapid, standard and universal way to evaluate the groundwater quality is the chemical analysis and its comparison with reference levels proposed or established by the scientific community, governments and international organisations.

REVIEW BY WATER CHARACTERISTICS AND ELEMENTS

General features

Organoleptic properties

Organoleptic properties of water are the result of the combination of dissolved substances, gases and the suspended materials. Colour, odour, taste and turbidity can be the reason of acceptance or rejection of water as a drink. Hence, these properties are very interesting because they act as a first (and of course, partial) quality control and health protection.

In general, groundwater does not have turbidity because suspended material is filtered by the rock during groundwater flow. Exceptions can be water from the karstified or fissured aquifers and from pumping wells without an adequate filter. Colour, odour and taste reflects the presence of organic matter, humic acids, iron, manganese, sulphurs, salt and other minor elements. Concerning the taste, there is a relationship between the quality of the taste and the total amount of solids in solution: very good (<300 mg/l), good (300-600 mg/l), acceptable (600-900 mg/l), poor (900-1200 mg/l) and unacceptable (>1200 mg/l) (World Health Organization, 1996). Similarly, water can be rejected due to its insipid taste if the mineralisation degree is too low.

Physico-chemical properties

Concerning the physico-chemical properties, groundwater has a very constant temperature derived from the average surface temperature plus the geothermal gradient down to extraction depth. The exception is the thermal water because they flow very quickly from deep locations to the surface following preferential paths. The normal groundwater pH ranges from 6.5 to 8. The normal values of temperature and pH do not have any undesirable effect on human health by themselves. In opposite, the importance of the physico-chemical properties lies in the fact that they are related with the chemical properties, that is, the dissolved substances. The solubility limits of many minerals depend on the temperature and the pH. Along the flowpath, if any of those properties changes, some solid phases can become unstable and dissolve and/or the solution can become oversaturated on those or other phases and lead to newly formed minerals. Those chemical reactions imply the change of the chemical composition of the groundwater along the flowpath.

Radiological aspects

Since the early years of the 20th century, it has been known that some natural waters are radioactive, especial-

ly those of certain thermal springs. Internal and external use of such water was once commonly believed to be beneficial for certain human ailments (Hem, 1985).

Radionuclides are present in all rocks in varying amounts, and they may be easily mobilised in the environment. Uranium, in particular, may be easily mobilized in ground water and surface water. As a result, uranium and its decay product, radium, enter the water supply through groundwater wells and surface-water streams and rivers. The health risks to humans are real, but the level of risk involved is not clearly defined because the distribution and concentration of these radionuclides is not sufficiently known (Otton, 1994).

Most drinking water sources have very low concentrations of radionuclides to be considered a public health concern. Nevertheless, naturally occurring uranium and the naturally occurring radium isotopes, ^{226}Ra and ^{228}Ra , have been observed to accumulate to levels of concern in drinking water sources (Environmental Protection Agency, 2000). Certain rock types contain trace amounts of the radioactive isotopes of uranium, thorium, and/or actinium. As these rocks are weathered, the resulting clays and other aquifer-forming materials may become a source of naturally-occurring radionuclides to drinking water sources. Other naturally occurring radionuclides include tritium, a beta particle emitter, which forms in the upper atmosphere. Natural tritium in groundwater tends not to occur at levels of concern.

^{222}Rn produced in the decay of ^{226}Ra has a half-life of 3.8 days and is the only radon isotope of importance in the environment. Radon is soluble in water and also can be transported in the gas phase. Many groundwaters contain readily detectable quantities of radon, which appear substantial in comparison with the accompanying dissolved-radium concentration. The radon in these waters is derived mostly from Ra in the solids in the aquifer. Rn is lost from solution by release to the atmosphere and by radioactive decay, and analyses generally must be performed in the field. The possible public health significance of ^{222}Rn in drinking water has not received much attention. Inhalation is the main path of incorporating radon. Where the water does not have opportunity to lose radon to the atmosphere, the concentration can substantially raise (Hem, 1985).

Whatever is the incorporation path, Rn is of concern because the daughter isotopes have a relatively long residence time in the human body, and as alpha emitters the organ containing the element absorbs all the radiation energy. Most of the naturally occurring radionuclides are alpha particle emitters (the uranium isotopes, ^{226}Ra and ^{222}Rn), but naturally occurring beta particle emitters also occur (^{228}Ra and ^{40}K).

The recommended reference level of committed effective dose is 0.1 mSv from 1 year's consumption of drinking-water (European Union, 1998). This reference level of dose represents less than 5% of the average effective dose attributable annually to natural background radiation. Below this reference level of dose, the water is acceptable for human consumption and action to reduce the radioactivity is not necessary. For practical purposes, the recommended guideline activity concentrations are 0.1 Bq/l for gross alpha and 1 Bq/l for gross beta activity (World Health Organization, 1996).

Microbiological aspects

Although it has been proved that the amount of underground microbiological mass is important in quantity and variety (Pedersen, 2000), there is no special concern about human health implications of naturally occurring micro-organisms in groundwater. In opposite, microbiological pollution of freshwater is one of the biggest problems all around the world and especially in developing countries.

Chemicals

In this section a review of the main chemicals of concern naturally occurring in groundwater and having an important health effect on humans is presented. Table 1 includes many other chemical elements than the ones described in the text.

Carbon

Inorganic carbon is abundant in most aquifer forming rocks and is one of the main constituents of sedimentary rocks, especially limestone. It is the most important dissolved compound in groundwater. This major compound has an atmospheric origin, like nitrogen, although soil can have high concentrations of both of them. Carbon is one of the main constituents of living beings. The most abundant chemical form under natural conditions is the bicarbonate anion. It is essential for health; no adverse effects are known.

Calcium

It is very variable in igneous rocks (<8%). It is the main component in limestone (30%) and very scarce in sandstone and clays (2.5-4%). The main minerals are calcite and aragonite. Calcium is very mobile under continental conditions and becomes a major component of water. Equilibrium with carbonates is the major mechanism in limiting the solubility of calcium in most natural water. It is essential for living beings and not only for the formation of the hard parts (skeleton).

TABLE 1 | Overview of the chemical elements naturally occurring in groundwater and essential and/or potentially toxic for humans.

Element ⁽¹⁾	Major/Trace	Essential	Potentially toxic	WHO guidelines (mg/l) (WHO, 1996)	EU guidelines (mg/l) (EU, 1998)	USEPA maximum contaminant level (mg/l) (EPA, 2002)	Average contents in natural groundwater ⁽²⁾ (mg/l)
C	M	x					1-100
Ca	M	x	x				15-45
Mg	M	x	x				4-11
Na	M	x	x		200		30-40
S	M	x	x		250	250	3-15
Cl	M	x	x		250	250	7-16
I	T	x					0.007-0.01
F	T	x	x	1.5	1.5	4	0.1-0.2
N	M	x	x	10	10	10	
Se	T	x	x	0.01	0.01	0.05	0.001
Mn	T	x	x	0.5	0.05	0.05	0.007-0.02
Fe	T	x			0.2	0.3	0.07-0.7
Cr	T	x	x	0.05	0.05	0.1	0.01
As	T		x	0.01	0.01	0.01	0.001
Hg	T		x	0.001	0.001	0.002	
Al	T		x	0.2	0.2	0.2	0.04-0.4
Pb	T		x	0.01	0.01		
Cd	T		x	0.003	0.005	0.005	
U	T		x	0.002		0.03	0.001
K*	M	x	x				2.5
Si*	M	x	x				8
P*	T	x	x				0.03
Ba*	T	x	x	0.7		2	
Be*	T	x	x			0.004	
B*	T	x	x	0.5	1		
Cu*	T	x	x	2		1	
Zn*	T	x	x			5	
Co*	T	x					
Ni*	T	x	x	0.02			
Mo*	T	x		0.07			
V*	T	x	x				
Sb*	T		x	0.005	0.005	0.006	

¹ Elements with the * mark have not been explicitly described in the text.

² This is an indicative range. Besides the references cited in the text, other general handbooks have been used (Custodio and Llamas, 1983; IEC, 1997)

Water hardness has been related with cardiovascular diseases (promoting or avoiding), even though, it is not clear if this relationship is due directly to calcium and/or magnesium or because metals are more soluble in hard waters (Edmunds and Smedley, 1996).

Magnesium

It is very abundant in mafic igneous rocks (23%) and its content decreases with acidity until 0.5%. Its average abundance in limestone is 4.7%, in clays 1.34% and sandstone 0.7%. It is a main compound in many minerals groups such as silicates, oxides, carbonates, sulphides and chlorides. Dolomite has a definite crystal structure in which calcium and magnesium ions are present in equal amounts.

Magnesium occurs in significant amounts in most limestones. The dissolution of this material obviously brings magnesium into solution, but the process is not readily reversible, that is, the precipitate that forms from a solution that has attacked a magnesian limestone may be nearly pure calcite. Magnesium concentration would tend to increase along the flow path of a ground water undergoing such processes, until a rather high Mg:Ca ratio is reached (Hem, 1985). It is very mobile under atmospheric conditions. It is also abundant in continental waters (4.1 mg/l average) and it is essential for living beings for the hard parts, organic fluids and chlorophyll.

Sodium

Its abundance in igneous rocks ranges from 0.5 to 4%, increasing with acidity. In limestone is below 2%. In clays ranges from 0.7 to 4% and in sandstone is 0.3% in average. There are a lot of sodium bearing minerals, mainly in the groups of silicates, halides and oxysalts. The most important mineral is halite, which is the most abundant salt. In silicates sodium forms isomorphic series with calcium and can be partially replaced by lithium. It is very soluble and extremely mobile in surface waters. Because of the high sodium concentrations that can be reached before any precipitate is formed, the sodium concentrations in natural water can have a very wide range. Sodium is adsorbed in clays and is the most important cation in hydrothermal fluids.

It is essential for living beings, for the organic fluids. An excess intake of sodium is related with high blood pressure.

Sulphur

In igneous rocks its abundance ranges from 200 to 400 mg/kg. Its average abundance in clays, limestone and sandstone is 0.1-0.3, 0.12 and 0.02% respectively.

Sulphur is the main component of many minerals from the groups of sulphides, sulphates and sulphosalts. The mineral sulphur (native) is also important. When sulphide minerals undergo weathering in contact with aerated water, the sulphur is oxidised to yield sulphate ions that go into solution.

Because this element occurs in oxidation states ranging all the way from S²⁻ to S⁶⁺, the chemical behaviour of sulphur is related strongly to redox properties of aqueous systems. In superficial conditions is very mobile (sulphates) under oxidising conditions but it is immobile under reducing conditions.

Groundwater flowing throughout evaporitic rocks such as gypsum can incorporate big amounts of sulphur as sulphate. Selenitic water is a natural water that has more than 500 mg/l of sulphate.

Natural waters subject to unusual conditions may attain high concentrations of hydrogen sulphide. Most people can detect the typical rotten-egg odour in waters that have only a few tenths of a milligram per litre of this substance in solution. Such waters are fairly common in association with petroleum. Sulphur is considered to be toxic or undesirable in excessive amounts (Edmunds and Smedley, 1996).

Chlorine

Chlorine content in igneous rocks increases with acidity and alkalinity and ranges from 70 to 520 mg/kg. The average content in sedimentary rocks is 160 mg/kg. Halite and other evaporitic chlorides are the most important minerals. It is concentrated in hydrothermal fluids. It is very mobile under superficial conditions and its average content in continental waters is 7-8 mg/l. The most important origin is rainwater and aerosols. The main dissolved form in groundwater is chloride, which is very stable and does not react with other species. Moreover it does not precipitate unless its concentration is very high (hundreds of grams per litre) (Custodio and Herrera, 2000).

Chlorine gas dissolves readily in water and has a somewhat stronger and more rapid oxidising effect than does dissolved oxygen. The element has long been used as a disinfectant or biocide in purification of water supplies.

Iodine

Iodine is one of the most important elements of concern related with health. It is scarce in igneous and metamorphic rocks (<0.5 mg/kg) and in clays, sandstone and limestone ranges from 1 to 1.7 mg/kg. The iodine minerals are very rare and they are formed under evaporitic (very arid) conditions. Iodine is found with sulphides, it is very mobile, it concentrates in organic matter and adsorbs onto iron and aluminium oxides.

The main source of iodine is seawater, from which it goes to the atmosphere and reaches the continent in form of wet or dry rain. For this reason it is more abundant in soil than in rocks and near the seaside than inland. In soils the iodine content increases with alkalinity and its chemical form depends on the redox potential (Fuge, 1996). In groundwater, the highest concentrations are found in calcareous aquifers (probably related with the organic matter contents). The contents in natural fresh water range from 0.01 to 70 µg/l (average 7 µg/l) depending on the topography (height, distance to the sea) and the kind of rain (Edmunds and Smedley, 1996).

Iodine is essential for human health because it is used to segregate the thyroidal hormone by the thyroid gland.

Only 20% of the iodine intake comes from water. The lack of iodine in the diet leads to the development of the goitre. The goitre is a benign tumour and consists in the increase of the size of the thyroid gland. The goitre is more abundant in rural areas, far from the sea and mainly in developing countries. Even though goitre can be promoted by the lack of other elements, it seems that this illness is related with the factors that immobilise iodine and prevent its uptake by humans (Fuge, 1996).

There are many studies of actual cases of goitre problems and groundwater iodine contents. Among them, we can point out the problems in Sri Lanka for its importance in terms of amount of affected people (Dissanayake and Chandrajith, 1996). Other illnesses can be related with the deficiency of iodine, such as death births, abortion, congenital deficiencies, cretinism and impaired mental functions. Among them cretinism is the most important (Stewart and Pharoah, 1996). Besides iodine, it seems that those diseases can have other geological origins. It appears that iodine deficiency disorders are found along many plate collision zones (Stewart and Pharoah, 1996).

There are guidelines concerning the minimum suitable iodine contents in drinking water but there are not guidelines for maximum allowed contents because no toxicity effects have been found (Edmunds and Smedley, 1996).

Fluorine

Fluorine is another of the most important elements of concern related with health. The fluoride content in igneous rocks increases with acidity and ranges from 100 mg/kg to 1200 mg/kg. Fluorine abundance in limestone ranges from 330 to 540 mg/kg, in sandstone is about 270 mg/kg and in clays ranges between 500 and 1300 mg/kg. The most important minerals are fluorite and apatite. Fluorine replaces O and OH in silicates. It is abundant in hydrothermal fluids (especially alkaline thermal water). Under superficial conditions is very mobile. Continental water can have concentrations up to 100 µg/l. Its concentration is naturally controlled by the solubility limits, saturation with fluorite. In general fluorine contents increase when the contents of As, Pb, Cd and Li increase and when the contents of Ca and Mg decrease (Carrillo-Rivera et al., 2002). Fluorine is essential for vertebrates because it is used as fluorapatite in the bones and teeth. Low concentrations in drinking water (< 0.5 mg/l, therefore, low intake dose) lead to dental caries (Edmunds and Smedley, 1996).

Health problems related with excess intake of fluorine usually emerge when abnormally low concentrations of associated ions (Ca) allow the concentration of fluorine to increase. If calcium in solution is reduced because, for instance, it exchanges with sodium, fluorite precipitation

is avoided. Concentrations higher than 2 to 4 mg/l lead to an exposure than can result in dental fluorosis and skeletal fluorosis respectively (Edmunds and Smedley, 1996). The effects are permanent and incurable. High fluorine concentration in drinking water has also been linked with cancer. Drinking water is not the only source of fluorine. The World Health Organization recommended contents for drinking water are 1.5 mg/l for low temperature water (8-12 °C) and 0.7 mg/l for naturally warm drinking water (25-30 °C).

Fluorine rich groundwaters, besides hydrothermal fluids, are located in granitic rocks and rift zones. There are many examples of health problems related with excessive fluorine in groundwater. In Sri Lanka a combination of factors derived from the geology, the climate and the social development have played a vital role in the health problems related with excessive fluorine intake (Disanayake, 1996).

A similar combination of those factors (geology, topography and climate) has led to a similar problem in a Mexican aquifer located in volcanic rocks. A proper management and an appropriate dilution with shallower water have been pointed as the solution to this local problem (Carrillo-Rivera et al., 2002).

Nitrogen

It is the main component of the atmosphere (78%). In igneous rocks ranges from 6 to 30 mg/kg and in clays the content is about 600 mg/kg. The only existing N bearing minerals are salts; sodium and potassium nitrates mainly. During the natural global cycle nitrogen takes several chemical forms. The most stable aqueous form in natural groundwater is the nitrate anion. Nevertheless, more reduced forms can exist if the environmental conditions are reducing enough (nitrites, molecular nitrogen, ammonia and ammonium).

Nitrogen is essential for living beings and a main constituent of biomass. The main source of N for humans is food.

Nitrate is a major concern in developed countries as a result of its potential health problems related with the excessive intake. Albeit most of nitrates come from diffuse agricultural pollution, in some places, the natural contents can be very important. In very arid regions, natural concentrations can exceed the recommended limits due to natural factors, for example fixation by leguminous plants or micro-organisms (Edmunds and Smedley, 1996).

Health effects of excessive nitrates or nitrites intake are the methaemoglobinaemia in children and stomach

cancer in adults. This children disease can lead to cyanosis and internal asphyxia. The most vulnerable populations are children and unweaned babies.

The most common maximum concentration allowed in drinking water is 50 mg/l nitrates. Many countries have higher limits (90-100 mg/l) albeit in this case that water can not be used for unweaned babies.

Ammonium can be the most abundant form of nitrogen form in very reducing environments (because the presence of humic acids, iron, etc.) and its concentrations can be naturally of several mg/l. No disease has been related with the excess of ammonium and ammonia in drinking water even if it affects, obviously, its organoleptic properties. While the World Health Organization gives a recommended maximum value for ammonia of 1.5 mg/l, the European Union set the maximum ammonium contents at 0.5 mg/l ammonium.

Selenium

Its abundance in clays is about 0.6 mg/kg and in the rest of the rocks is less than 0.1 mg/kg. It is found in rare minerals and as native selenium. Often it replaces sulphur in sulphide and sulphates because its geochemistry is similar. Selenium is found in hydrothermal deposits of sulphides and uranium deposits. Its mobility increases with pH and in reducing media. The mobility and toxicity depends on the oxidation state.

Selenium is an essential element for human health but very toxic in excess. Selenium deficiency may promote muscular degeneration, impeded growth, fertility disorders, anaemia, liver diseases and the Keshan diseases (chronic cardiomyopathy) (Edmunds and Smedley, 1996; Siegel, 2002).

The excess of selenium intake (>10 mg per day) can lead to health problems such as gastro-intestinal ailments, skin discoloration and tooth decay (Edmunds and Smedley, 1996). Other related diseases are haemorrhages and circulatory disorders, chronic dermatitis, lose of hear, icteric and caries (Siegel, 2002).

Manganese

Its content in igneous rocks varies between 0.2% (ultramafic) and 0.06% (acidic). As average, limestone has 0.11%, clays 0.07% and sandstone 30 mg/kg. Manganese bearing minerals are scarce. It can replace iron in many silicates and calcium in carbonates. It is not very mobile under superficial conditions. Solubility, mobility and speciation are extremely related to the redox state of the system. Manganese is less mobile under oxidising conditions and under alkaline conditions. Under reducing

conditions the water concentrations can reach several mg/l, however, the average content in continental water is 7 µg/l.

Manganese is essential for living beings and it is readily absorbed. There is limited evidence that it may be toxic (neurotoxic effects) at high concentrations. Elevated contents of manganese affect the organoleptic properties of water.

Iron

The iron contents in igneous rocks increase with alkalinity and range between 21.7% and 10%. Clays have 3-5% and sandstone and limestone less than 1%. Iron is the main component of many minerals: silicates, sulphides, oxides and oxisalts. In sedimentary environments iron concentrates in oxidised formations and in sulphide rich formations. Its mobility increases in reducing media and when pH decreases. Its solubility, mobility and speciation are strongly dependent on the redox state of the system.

Iron is essential for humans. Elevated contents of iron affect the organoleptic properties of water.

Chromium

The ultramafic igneous rocks are higher in chromium content than other rock types (1800 mg/kg). Limestones have an average content of 11 mg/kg, sandstones 35 mg/kg and clays 95 mg/kg. The most important mineral is chromite that may be concentrated in lateritic residues overlying ultramafic rocks. Chromite is highly resistant to weathering. Chromium bearing minerals are scarce; it can replace iron and aluminium in silicates and has a very low mobility under superficial conditions. It is absorbed onto clays and iron and manganese oxides. The most abundant species in solution are those with oxidation state of +3 and +6, being the last one the most mobile in the environment and the most readily absorbed by human body.

Concentrations of chromium in natural waters that have not been affected by waste disposal are commonly less than 10 µg/l (Hem, 1985).

Chromium is an essential element (Siegel, 2002). In general, food appears to be the major source of chromium intake but drinking water and inhalations are also important paths. Chromium (VI) is considered as human carcinogenic. As a practical measure, 0.05 mg/l of total chromium is considered to be unlikely to give rise to significant risks to health (World Health Organization, 1996).

Arsenic

Arsenic contents in igneous rocks range between 1 and 2.5 mg/kg, in clayey sediments between 7 and 13 mg/kg and its abundance in limestone is less than 1 mg/kg.

A lot of minerals can contain arsenic as a trace element. It is mainly found with sulphides (orpiment, arsenopyrite, realgar, enargite) and coal (0.2%). Under superficial conditions is very mobile. Its especiation (and therefore its mobility and toxicity) depends on the redox state of the system.

Arsenic species in aqueous systems consist principally of arsenite (+3) and arsenate (+5) ions, being the last one more mobile and less toxic than the former (Bocanegra et al., 2002). These species are highly soluble over a wide range of Eh and pH conditions. However, under reducing conditions in the presence of sulphide, arsenic mobility is reduced due to the precipitation of minerals. Arsenic is strongly sorbed onto ferric hydroxide and also onto aluminium hydroxide.

Occurrences of high arsenic in drinking water are relatively rare. Most recorded cases are associated with sources of natural sulphide minerals, most notably pyrite and arsenopyrite, and these are often exacerbated by sulphide-mining activities (Edmunds and Smedley, 1996; Smedley et al., 1996). On the other hand, abnormally high arsenic contents in groundwater can also be found in other geological context (Warner, 2001).

The concentration of As in unpolluted fresh water typically ranges from 1-10 µg/l, rising to 0.1-5 mg/l in areas of sulphide mineralisations and mining (Thornton, 1996).

Arsenic is toxic and carcinogen. Its toxicity depends on the oxidation state and on the chemical form (organic or inorganic). Reduced forms are more toxic. Arsenic intake by humans is probably greater from food than from drinking water. Notwithstanding drinking water represents by far the greatest hazard since the species present in groundwater are predominantly the more toxic inorganic forms. The maximum recommended inorganic arsenic intake is 2 µg per day and kg of body weight (Thornton, 1996). A chronic exposure to arsenic can lead to skin diseases (skin alteration, hyperpigmentation, depigmentation), stomach-ache, neurological and cardiovascular alterations and the apparition of carcinomas and malign tumours.

Arsenic is one of the most important elements of concern and there are a lot of works and studies concerning

its behaviour and implications on human health. The potential presence of arsenic in many hydrogeological scenarios, its redox controlled mobility and its severe effects on the human health lead to the necessity of making regular controls in all public water supplies. The maximum recommended concentration of total arsenic in drinking water by several organisms is 10 $\mu\text{g/l}$.

Among the naturally occurring toxic elements in groundwater, arsenic is probably the most known and present in a higher number of countries (Table 2). Countries having the biggest problems and number of studies are Argentina, Chile, USA, Taiwan, China and Mexico, and affecting to a bigger number of people, Bangladesh and India. Among them, probably, the most important case is the groundwater arsenic problem in Bangladesh widely studied and reported during several years by the British Geological Survey.

Mercury

Clays can have concentrations up to 350 $\mu\text{g/kg}$ of mercury; the rest of rocks and soils usually have less than 40 $\mu\text{g/kg}$. Cinnabar is the most important mineral but mercury can also be present in other sulphides replacing Cd, Ag or Pb. Under superficial conditions mercury is very mobile. Mobility increases in acidic and oxidant environments.

The average mercury content in continental water is 0.007 $\mu\text{g/l}$ and in general it is not found in natural groundwater. Only very particular geological situations

(hydrogeological scenario) can lead to abnormally high mercury contents in groundwater, close to important sulphide mineralisations or with important volcanic activity.

Although almost all mercury in the environment comes from pollution and the most important intake is by food, high background mercury contents have been found in Japan and USA (Siegel, 2002). This has led to establish a maximum recommended concentration for drinking water of 1 $\mu\text{g/l}$.

Mercury is very toxic for living beings. The main exposition path for humans is ingestion of contaminated (enriched) food (vegetables, fish). Nevertheless, drinking water, dermal contact and inhalation can also be important exposure paths.

Aluminium

Aluminium is the third most abundant element in the earth's crust. It is a major component of aluminosilicate minerals and therefore very abundant in most rocks. Igneous rocks have concentrations between 0.5 (ultramaphic) and 7%. Clays have always more than 7% and limestone and sandstone less than 2.5%.

Its solubility and mobility are strongly related to environmental pH. Important concentrations are only found at pH below 5.5. It can be related to colloids and suspended particles that contribute to total aluminium contents but that are not detected in the microfiltered water samples.

TABLE 2 | Overview of the main incidence or arsenic in natural water around the world (modified from Nordstrom, 2002).

Country/region	Potential exposed population	Concentration ($\mu\text{g/l}$)	Environmental conditions
Bangladesh	30,000,000	<1 to 2,500	Natural; alluvial/deltaic sediments with high phosphate
West Bengal, India	6,000,000	<10 to 3,200	Similar to Bangladesh
Vietnam	>1,000,000	1 to 3,050	Natural; alluvial sediments
Taiwan	100,000 to 200,000	10 to 1,820	Natural; coastal zones, black shales
Inner Mongolia	100,000 to 600,000	<1 to 2,400	Natural; alluvial and lake sediments; high alkalinity
Xinjiang, Shanxi	>500	40 to 750	Natural; alluvial sediments
Argentina	2,000,000	<1 to 9,900	Natural; loess and volcanic rocks, thermal springs; high alkalinity
Chile*	400,000	100 to 1,000	Natural volcanogenic sediments; closed basin lakes, thermal springs
Bolivia	50,000	–	Natural; similar to Chile and parts of Argentina
Mexico*	400,000	8 to 620	Natural; volcanic sediments, mining
Germany	–	<10 to 150	Natural: mineralized sandstone
Hungary, Romania	400,000	<2 to 176	Natural; alluvial sediments; organics
Spain	>50,000	<1 to 100	Natural; alluvial sediments
Greece*	150,000	–	Natural; thermal springs and mining
Ghana*	<100,000	<1 to 175	Natural; gold mining
USA and Canada*	–	<1 to >100,000	Natural; thermal springs, alluvial, closed basin lakes, various rocks

*Also artificially enhanced arsenic contents

Only a small amount (4%) of the total aluminium intake is by drinking water (Smith et al., 1996) but the greater bioavailability of aluminium in drinking water may therefore render it a relative more harmful source than food (Edmunds and Smedley, 1996). It seems that a prolonged exposure to high aluminium intakes leads to the development of Alzheimer's disease.

Health effects due to the excess aluminium intake by drinking water are still not clear. Moreover, it is difficult to establish a guideline because aluminium is used in water treatment plants. The World Health Organization guideline of 0.2 mg/l is based on a compromise between reducing aesthetic problems and retaining the efficacy of water treatment. A systematic study carried out in Uganda illustrates the complexity of the collection and interpretation of analytical data on which to base epidemiological studies of Al excess/deficiency (Smith et al., 1996).

Lead

Lead is present as a major element in galena and is a common constituent in hydrothermal mineral veins. Its average crustal abundance is 16 mg/kg. Lead solubility is controlled principally by carbonate. Concentration in water can increase when the alkalinity and pH decreases.

Natural water rarely exceeds 10 µg/l, the World Health Organization maximum recommended level. The maximum concentrations found in water are related with acidic water (Edmunds and Smedley, 1996).

Lead is not essential and is toxic (Siegel, 2002). Environmental Protection Agency estimates that approximately 20% of human exposure to lead is attributable to lead in drinking water. Lead is a cumulative poison initiating tiredness, irritability, anaemia, behavioural changes and impairment of intellectual functions.

Cadmium

Cadmium abundance in igneous rocks ranges from 0.1 mg/kg in acidic rocks to 0.2 mg/kg in alkaline rocks. Limestone and sandstone have only between 0.03 and 0.05 mg/kg. Clays are enriched in cadmium having 0.3-0.4 mg/kg. Cadmium bearing minerals are rare. Cadmium is associated with zinc in sulphides and silicates and can replace lead in sulphides. Cadmium mobility under superficial conditions is low. It concentrates in sedimentary reducing environments and with the presence of sulphides. Cadmium solubility is controlled by carbonate and therefore, increases with acidity. Cadmium sorbs onto organic matter. Natural groundwater often has low cadmium contents unless volcanic exhalations affect it.

Cadmium is not an essential element and is toxic and

carcinogen (Siegel, 2002). The main intake is by food ingestion and air inhalation.

Cadmium interferes with zinc in enzyme catalysis and key metabolic processes and zinc bioavailability. As an acute toxin, the excess intake of cadmium leads to symptoms such as giddiness, vomiting, respiratory difficulties, cramps and loss of consciousness. Chronic exposure to the metal can lead to anaemia, anosmia, cardiovascular diseases, renal problems and hypertension. There is also evidence that increased cadmium ingestion can promote copper and zinc deficiency in humans, both necessary elements in metabolic processes.

Uranium

For uranium, we must consider not only the carcinogenic health effects from its radioactive decay and the decay of its daughter products (radiotoxicity), but also damage to the kidneys from exposure to the uranium itself (chemical toxicity).

Uranium is present in concentrations between 0.1 and 10 µg/l in most natural water. Concentrations greater than 1 mg/l can occur in water associated with uranium-ore deposits (Hem, 1985). Exposure to elevated uranium levels in drinking water has been shown to lead to changes in kidney function that are indicators of potential future kidney failure (Environmental Protection Agency, 2000).

Therapeutic water

The therapeutic effect of some groundwaters, usually thermal and mineral water, over the human body is well known from long ago. This type of water is called mineromedicinal water. Every country has its own regulatory system for designating the different types of water and their use. In order to designate a given water as a mineromedicinal water it has to accomplish a set of requisites. Among those requirements, natural springs need to have a minimum flow rate with chemical composition constant with time. Moreover, therapeutic properties have to be demonstrated by scientific studies (medical hydrology). The use of that water for health purposes is known as watertherapy, hydrotherapy, crenotherapy, spatherapy, thalassotherapy, etc.

Therapeutic water must be used always under medical control and can be used on site or far away from the surge. On site one can take benefit from physico-chemical properties that are lost if water is bottled and transported. Among these properties are water temperature (hot or cold), dissolved gases and chemical species unstable under superficial conditions.

Therapeutic actions of water can be physical by

means of body baths (either systemic application or local application) and/or biochemical by means of inhalation or ingestion. Physical actions are the lightness sensation when the body is submerged, and the compressive effect over blood vessels, skin and muscles. Moreover, water temperature activates the physiological mechanisms to keep the body's temperature when hot water (thermotherapy) or cool water (cryotherapy) is applied (Mitjà, 1999).

Physicochemical properties and chemical composition determine therapeutic properties of mineromedicinal water. If the temperature of that water in the spring is always at least 4°C above the average atmospheric temperature, then they are also called thermal water and hot springs.

Mineromedicinal water can be classed following many different criteria. Some of those criteria are the geological context, the physicochemical properties (T, TDS, amount of anions and cations, osmotic relation with body fluids), the therapeutic effects (laxative, purgative, tonic, exciting, etc.), the use (ingestion, inhalation, topic, etc.). A classification based on the relative abundance of the chemical elements is presented in Table 3.

The classification based on the abundance of the major anions and/or cations, with variations, is the one used in hydrotherapy and medical hydrology. Scientific progress in water analysis technology and in medicine will progressively improve the knowledge of therapeutic effects on human health of water physicochemical properties.

TABLE 3 | Different mineromedicinal water groups and its therapeutic properties (De Armijo Valenzuela, 1968).

Main group	Subgroup	Application
Sulphide	Na Ca	Rheum, allergy Intoxication, inflammations
Cl	S I Na	Metabolic Catarrh Inflammations
Sulphate	Na Mg	Collagen Purgative
Bicarbonate	gassy Na	Dyspepsia, antacid Congestion
Ca	Bicarbonate Sulphate	Allergy, sedative Inflammations
Fe		Anaemia, restorative
Trace metals	Hot Cold	Catabolism stimulant Diuretic
Radioactive	N no N	Equilibrate, sedative Catarrh

A synthesis of the physicochemical water properties and therapeutic effect on the human health is presented below (De Aminjo Valenzuela, 1968; Mitjà, 1999):

Bicarbonate: antacid and diuretic. Enhance pancreas secretion. Effects on gastrointestinal system and metabolic diseases.

Sulphated: purgative, cholagogue, laxative, etc.

Chlorided: cholagogue, metabolism stimulation.

Sulphided: antitoxic, antiseptic, respiratory affection, dermatosis.

Ferrogenous: astringent. Hyposidiremy, ferropenic anaemia.

Carbonic: diuretic action, they stimulate secretion and gastric mobility.

Oligometalic waters: with low mineralisation (TDS < 100 mg/l). Hypotonic and diuretic (without any cardiovascular or renal problems).

The presence of some trace elements in groundwater causes its therapeutic properties, which are in general beneficial for human health; these often are essential elements. The study of the role of microelements on pathologic processes, together with the geochemical scientific progress, leads to a new discipline, the medical geochemistry, parallel to medical hydrology (Komatina and Komatina, 2002). Examples of these topics are the study of the role of zinc on protein syntheses, of copper on collagen-elastine syntheses, of molybdenum on aminoacid metabolism, of selenium as antioxydant and in immunologic functions, and of many others as it has been described in the preceding sections.

CONCLUSIONS

Groundwater is widely used for freshwater supply. Besides the artificial pollution, the natural quality of groundwater is not always suitable. Human health depends on water from a qualitative and quantitative point of view. Water plays two roles in human health; on one hand it is ingested as a drink, prepared beverages or food. On the other hand water has an important social use in the individual and communities hygiene. The main concern derived from natural groundwater quality is related with the former use.

Many elements naturally occurring in groundwater can also be ingested (incorporated) by food, inhalation or dermal contact. Hence, it is necessary to talk about doses and not only concentrations. Despite the difficulty of measuring, controlling and writing guidelines on doses (minimal and maximal), they are more meaningful than concentrations because they are directly linked to the toxicity and the risk assessment.

Natural groundwater can have a lot of different chemical elements, albeit most of them in very small amounts. Natural composition of groundwater depends on its hydrogeological scenario. Each scenario is characterised by a set of factors that can be grouped into three categories; geology, climate and topography. Rock forming minerals are the source of most chemical elements in groundwater. An acceptable abundance of major groundwater compounds is expected from igneous and metamorphic rocks, which are found as substrate in many developing countries, fluoride, iron, manganese and aluminium can be of concern. Its abundance is controlled by mineral solubility and concentration of cations, or by the oxidation state.

The main aquifers in terms of yield are located in big sedimentary basins. The main geological formations are sandstone and limestone. In these aquifers, the groundwater quality distribution is related to the residence time, depth and distance to the sea. Sandstone and conglomerate are permeable and may, therefore, easily receive and transmit solutes acquired by water from some other type of rock. Moreover, alteration processes may influence the composition of circulated water. Water from sandstone and conglomerates has a wide range of chemical quality.

Many sediments form in anaerobic environments and contain organic material or other solids that can maintain reducing conditions for long periods of time. The solutions moving through the sedimentary rock may bring oxygen and oxidise the reduced species, mobilising iron and sulphur.

Groundwater associated with pure quartz sand can be among the lowest in dissolved solids content of any groundwater. Clay minerals can have high cation-exchange capacities and may exert a considerable influence on the concentrations of the different cations in water associated with them.

Salt derived elements such as sodium, calcium, magnesium, chlorine, sulphur as well as iron and aluminium can be of concern when groundwater comes from this kind of geological formation.

Limestone and dolomite form very important aquifers from both a quantitative and qualitative point of view. Calcium, magnesium and bicarbonate are invariably the most important ions. Water hardness is an widespread but not critical problem.

The chemical elements present in natural groundwater of more concern for human health are those located simultaneously into the three following categories: its intake from drinking water is highly significant, anomalous concentrations are found in many areas world-wide

and its insufficient and/or excessive intake lead irrevocably to critical illness. Among those elements we can highlight fluorine and arsenic. An insufficient intake of fluorine produces dental caries. In opposite, high fluorine intake leads to painful-skeleton deformations termed fluorosis. This disease is common in African Rift Valley countries, where sources of fluorine are important, and in India and West Africa where salts and sedimentary fluorine-bearing minerals are the primary sources. Elevated arsenic concentrations are commonly associated with sediments partially derived from acidic volcanic rocks. Arsenic is also associated with sulphides, and high concentrations can sometimes be found in water that also contains appreciable iron concentrations.

The effects of natural groundwater composition on human health are being studied from a long time ago and the health effects of most chemical elements are fairly known. Despite that, the increasing use of groundwater, the wish of improving the health status in developing countries and the need of relating health effects to intake doses imply that this subject is of continuous interest for the scientific community.

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