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Assessment of Groundwater Quality in Village Pepaj, Rugova Region, Kosova

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Abstract: Supply of safe, clean and abundant water for drinking purposes is essential for good health. The aim of this study was to assess the groundwater quality in village Pepaj, Rugova Region by analysing physico-chemical parameters, major and trace elements. Groundwater samples taken from tube-well were analysed for temperature, pH, dissolved oxygen, conductivity, total dissolved solids, total hardness, bicarbonate, ammonia, nitrate, phosphate, sulphate, chloride and fluoride. The concentrations of major and trace elements such as Ca, Mg, K, Na, Mn, Mo, Co, Fe, Zn, Se, Ni, Cu, Cr, Al, Sr, Sb, Ba, Cd, As, Hg and Pb were determined by Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES). The mean concentration of the anions follows the order: HCO_3^- >SO_4^{2-} >NO_3^- >NH_4^+ >Cl^- > F^-. The concentrations of Ca, Mg, K, Mn, Fe, Zn, Cu, Cr, Al and Ba were found to be within the drinking water standards of the World Health Organization, European Union (98/83/EC Directive) and US Environmental Protection Agency. While Na, Mo, Co, Se, Ni, Sr, Sb, Cd, As, Hg and Pb were not detected in any of the analysed samples. The findings revealed that there was no public health risk in view of physico-chemical, major and trace elements concentrations in groundwater.

Keywords: *Rugova Mountain Region, physico-chemical parameters, major and trace elements, groundwater, drinking water quality, ICP-OES*

Introduction

Supply of safe, clean and abundant water for drinking purposes is essential for good health. Groundwater is a very valuable natural resource and plays a key role in sustainable development in many countries around the world. Groundwater differs substantially from surface water in many characteristics. It is located beneath the earth's surface in soil pore spaces and in the fractures of rock formations. Groundwater presumed to be naturally protected, it is considered to be free from impurities, which are associated with surface water, because it comes from deeper parts of the earth. Its quality is significantly affected by geologic formations of aquifers as well as by anthropogenic activities (Thomas, 2000). The composition and concentration of substances in groundwater is a resultant of the geological structure of the earth's crust, chemical composition of the underlying rocks, soil formation and the length of time that the water body has been trapped underground (Jennings, 1996) and anthropogenic activity associated with agriculture, industry and public utilities.

Rugova Region is located far away from many pollutant factors, mining and agricultural activities which adversely affect the groundwater quality. Groundwater chemistry is influenced by geology, chemical composition of the underlying rocks, lithologic effects, climate, groundwater flow and anthropogenic activities. The major and trace elements such as Ca, Mg, K, Na, Mn, Mo, Co, Fe, Zn, Cu, Cr and Se are essential nutrients, however, an excess amount of such elements produces cellular and tissue damage leading to a variety of adverse effects and human diseases. Other elements such as Al, Ba, Sr, Sb, Cd, As, Hg and Pb have no established biological functions and are considered as non-essential metals. Because of their high degree of toxicity and carcinogenicity Cd, As, Hg and Pb, rank among the priority metals that are of public health significance (Chang *et al*., 1996).

Recently, due to less availability a high quality of natural spring water near by their homes, some families of Rugova Region drill tube-wells and use groundwater as their source of fresh water for drinking and other domestic purposes. They use the groundwater for drinking water without analyses their water quality. Therefore, the objective of this study was to assess groundwater quality in village Pepaj, Rugova by analysing physico-chemical parameters, major and trace elements.

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Materials and Methods

General description of sampling site

Groundwater samples were collected from tube-well in village Pepaj, Rugova Region, Kosova. Rugova is a mountain region located in the north-western part of Kosova. It is a region within "Bjeshkët e Nemuna", also known as the Albanian Alps. Rugova is at latitude of 42°44' N and a longitude of 20°3' E, and it is 93 km from Prishtina, the capital of Kosova. The highest peak is Hajla at 2403 m. Rugova has a wet, continental climate that is influenced by the mountains, short and hot summers and long and harsh winters. Spring is late, and the seasons change quickly. The high level of precipitation is a result of clashes between the tropical and continental climates. The annual minimum and maximum precipitation are 540.6 ml and 1336 ml, respectively (Natyra e Rugovës, 2001).

Geology of the Study Area

The sampling site lies between the latitudes X-428344 and longitudes Y-4731496 and elevation of 1643 m (figure 1), determined by using a GPS type (GARMIN GPSmap 62).

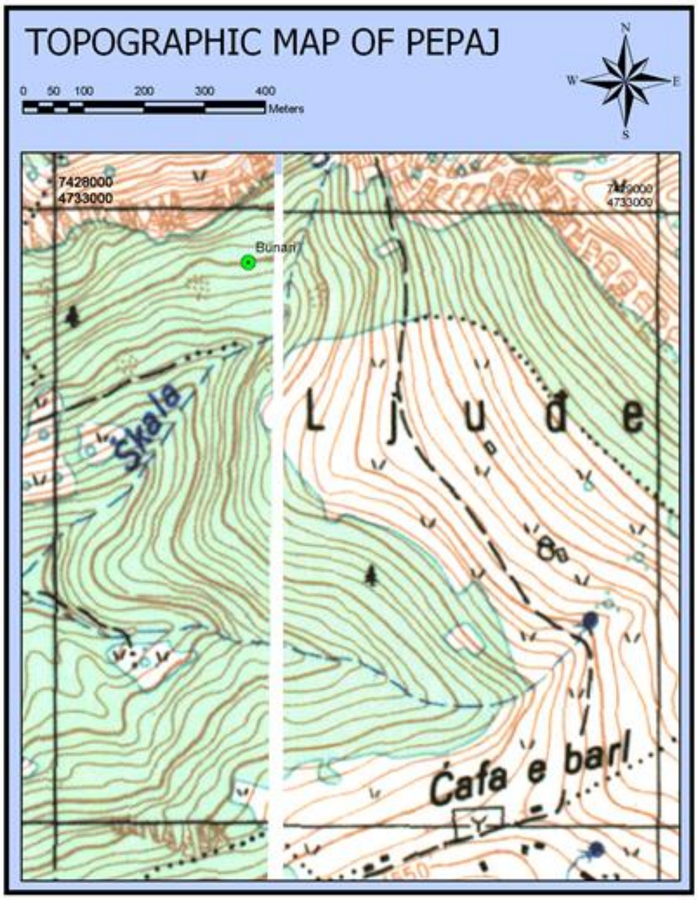

Figure 1. Map depicts topography and location of the groundwater studied, village Pepaj, Rugova

The first research on geological composition of the region was conducted in the early twentieth century. These were mainly the research work of the Dinarides tectonic, lithological composition and stratigraphic. The area where the study was conducted spread on the palaeozoic, triassic and quaternary formations. Palaeozoic formations are spread in the southern part, on Sharri Mountains in the west, and in the north in the shape of a band that is few kilometres long. These formations are composed of schist, quartzite, sandstone, limestone and conglomerates. Triassic formations are represented mainly by limestone and dolomite which are over 600 m thick, which are formed in quiet conditions of sedimentation. Limestones are tectonically destroyed, with lot of cracks and seams. The network density of these cracks sometimes favours erosion and karst processes which in their turn serve as a way for the passage of groundwater (Antonjevic *et.al*., 1978). Quaternary sediments are widespread in this region. Pleistocene and Holocene sediments are found in this region as well represented by glacial and fluvioglacial while proluvium formations, deluvium and alluvium have greater spread along the valley.

Sampling, physico-chemical, major and trace elements analyses

The groundwater samples were collected in village Pepaj from deep aquifer tube-well during October 2016 for physico-chemical, major and trace elements examinations. This is the only well in village Pepaj and its depth is 118 m. Water samples from tube-well were collected after running the water for about 15-20 min. The pre-washed plastic bottles of one liter were rinsed thrice with water samples on the site before sample collection. The physico-chemical parameter such as pH, temperature electrical conductivity and dissolved oxygen (DO) were measured in situ in the field using Hanna model multiparameter probe (HI 991301) and DO meter model (HI9147). In meantime the collected samples were stored in cool box and transported to N.SH. Agrovet Laboratory, Prishtina and analysed immediately following the protocol of standard methods (APHA, 2005). Total hardness was determined by EDTA volumetric titration (Standard Method 2340C). Bicarbonate (HCO_3^-) was determined by acid titration, with methyl orange as indicator. Ammonia (NH_4^+), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), chloride (Cl^-) and fluoride (F^-) were measured using spectrophotometer model HACH DR 3900 (Standard Methods US EPA: 8155, 8192, 8048, 8051, 8113 and 10225).

Separate water samples were also collected for major and trace elements analysis, in high-density polyethylene bottles of one litter capacity. Prior to collection, the bottles were washed with distilled water and subsequently rinsed thoroughly with the sample water. For validation of results, three water samples were collected at every sampling. Collected samples were immediately acidified in the field to pH <2.0 by adding HNO_3. In meantime the collected samples were stored in cool box and transported to N.SH. Agrovet Laboratory, Prishtina. Water samples were preserved according to standard procedures (APHA, 2005). The concentrations of major and trace elements such as Ca, Mg, K, Na, Mn, Mo, Co, Fe, Zn, Se, Ni, Cu, Cr, Al, Sr, Sb, Ba, Cd, As, Hg and Pb were determined by Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP–OES Optima 2100 DV) in accordance with the standard methods 3015A (US EPA, 1994) and 6010C (US EPA, 2007). Limits of detection (LOD) of some elements were as follows: As (0.002 mg/l), Cd (0.0001 mg/l), Co (0.0002 mg/l), Cr (0.0002 mg/l), Cu (0.0004 mg/l), Hg (0.001 mg/l), Mn (0.0001mg/l), Mo (0.0005 mg/l), Na (0.0005 mg/l), Ni (0.0005 mg/l), Pb (0.001 mg/l), Sb (0.002 mg/l), Se (0.004 mg/l), Sr (0.00005 mg/l) and Zn (0.0002 mg/l). Tests were undertaken in duplicate and the results averaged to reduce experimental errors.

Results and Discussion

Physico-chemical properties of groundwater

The mean values of physico-chemical parameters of groundwater samples collected from tube-well in village Pepaj, Rugova are summarized in table 1. Groundwater samples collected from tube-well have crystal clear appearances, a good taste and were odourless. The groundwater quality results were compared to the maximum values recommended by EU (98/83/EC Directive, 1998), World Health Organization (WHO, 2008) and US Environmental Protection Agency (US EPA, 2012) standards.

Water temperature and pH are important factors that affect the taste of water. Temperature has been known to have effects on other parameters, speed of chemical reactions, dissolved oxygen, conductivity, pH and compound toxicity. The solubility of oxygen and other gases will decrease as temperature increases while a high water temperature increases the solubility and thus toxicity of certain compounds (Bhadja & Vaghela, 2013). The mean temperature of groundwater samples was 9.4 °C, which is within standard limit. The pH of most natural waters range from 6.5-8.5 which is a deviation from neutral 7.0 as a result of the CO_2/bicarbonate equilibrium. The mean pH value of groundwater samples was 7.02, which is within permissible standards limit. The pH may affect the solubility and bioavailability of other chemical elements in water (Hem, 1985). Dissolved oxygen (DO) is often used as an indicator of water quality, such that high concentrations of oxygen usually indicate good water quality. DO enter in water by diffusion from the atmosphere and as a by-product of photosynthesis by algae and plants. DO in water is inversely proportional to the temperature of the water; as temperature increases, the amount of dissolved oxygen decreases. The mean DO value of groundwater samples was 8.3 mg/l, which is within permissible WHO (2008) limits.

Electrical conductivity (EC) is the ability of the water to conduct electricity and is directly related to the concentration of ions and on the temperature of the liquid. The mean EC value of groundwater samples was 430 μs/cm, which is within permissible standards (table 1). Karst groundwater is typically dominated by bicarbonate ions due to the calcium carbonate bedrock. Total dissolved solids (TDS) comprise minerals, salts, metals, cations or anions dissolved in water. TDS in drinking water originate from natural sources, sewage, urban run-off, and chemicals used in the water treatment process. The mean TDS value of groundwater samples was 275 mg/l which is within permissible standards. Low TDS values can be caused by natural filtering performed by the rock through groundwater rocks, which is a good agent to conduct groundwater filtration (Freez & Cherry, 1979). Elevated TDS indicate that the dissolved ions may cause the water to be corrosive, of salty or brackish taste, resulting in scale formation.

Table 1. The mean values of physico-chemical parameters of groundwater samples in the village Pepaj, Rugova

Parameters	Groundwater	EU (1998)	WHO (2008)	USEPA (2012)
Temperature, (^oC)	9.4	25	-	-
pH	7.02	6.5-9.5	6.5-8.5	6.5 - 8.5
Dissolved oxygen, mg/l	8.3	-	≥6	-
Conductivity, μS/cm	430	2.500	1500	2500
Total dissolved solids, mg/l	275	-	600	500
Total hardness, ^{o}dH	15.68	-	-	-
Bicarbonate, mg/l	280	-	500	-
Ammonia, mg/l	0.177	0.5	1.5	0.30
Nitrate, mg/l,	1.53	50	50	10
Phosphate, mg/l	ND	-	0.1	-
Sulphate, mg/l	5	250	250	250
Chloride, mg/l	0.1	250	250	250
Fluoride, mg/l	0.09	1.5	1.5	0.8

Water hardness is usually due to the presence of multivalent metal ions, which come from minerals dissolved in the water especially Ca and Mg. Classification of water hardness in German degrees is: soft (less than 8.4 °dH), medium (8.4-14 °dH), hard (14-20 °dH) and very hard (more than 20 °dH). The mean total hardness values of groundwater samples was 15.68 °dH. Based on these result, the groundwater is generally hard. This hardness is the result of limestone and dolomite in the local geology. No health effect has been associated with hardness in drinking water. Hard drinking water generally contributes a small amount toward total calcium and magnesium human dietary needs. Total hardness can have a protective effect against heart disease or an inverse relation with cardiovascular diseases in general (Tebbutt, 1998). The mean bicarbonate (HCO_3^-) concentration of the groundwater samples was 280 mg/l, which is within safe limits of WHO (2008) standard. A high concentration of bicarbonates in drinking water is deviated by weathering of calcium bearing rocks. Carbonates such as limestone, dolomite and calcite dissolve to form bicarbonates by the action of CO_2 derived from rain.

The mean concentration of ammonia (NH_4^-) of the groundwater samples was 0.177 mg/l. The concentration of ammonia was less than permissible standards limits (table 1). Ammonia is of no direct importance to health in the concentrations that can normally be expected in drinking water. In uncontaminated surface water, the value of ammonia is usually less than 0.2 mg/l. Intensive rearing of farm animals can give rise to much higher levels in surface water. Nitrate concentration in surface and groundwater is normally low, but can reach high levels as a result of agricultural runoff, agricultural activities and contamination by human and animal wastes (Lajçi *at al*., 2016). It is regarded as an indicator of pollution in public water supply. The mean nitrate (NO_3^-) concentration of the groundwater samples was 1.53 mg/l, which is lower than permissible standards (table 1). Nitrogen is essential for all living things as it is a component of protein. However, excessive concentrations of nitrate-nitrogen in drinking water can be hazardous to health, especially for infants and pregnant women (Ward *et al*., 2005). Water may contain phosphate (PO_4^{3-}) derived from contact with natural minerals or through pollution from an application of fertilizer, sewage and industrial waste. Phosphate was not detected in groundwater samples. Phosphate is toxic to animals and humans at extremely high levels and could cause digestive problems (Ijeh & Onu, 2013).

Sulphates (SO_4^{2-}) occur naturally in numerous minerals, including barite, epsomite and gypsum. The sources of sulphate in surface and subsurface water are mainly calcium sulphate and sodium sulphate. The mean sulphate concentration in analysed groundwater samples was 5 mg/l, which is lower than permissible standards (table 1). High levels of sulphate lead to dehydration and diarrhoea especially in children and produce a bitter taste (WHO, 2008). Chloride (Cl^-) may present naturally in groundwater and may also originate from diverse sources such as weathering, leaching of sedimentary rocks and infiltration of seawater etc. The mean chloride concentration in groundwater samples was 0.1 mg/l, which is below the standard limits (table 1). Chloride is not harmful to human at low concentration but at high content cause cardiovascular problem and give a bitter taste (Terrence *at al*., 2007). Fluoride (F^-) is a trace element important for human health and is obtained primarily through consumption of water. Higher concentration of fluoride causes bone and dental fluorosis. The mean concentration of fluoride in groundwater samples was 0.09 mg/l which is within permissible limits (table 1). The fluoride concentrations in natural ground waters vary with geological composition of rocks (Khaiwal, 2006).

Major and trace elements of groundwater

Major and trace elements are introduced into the aquatic system through several ways which include weathering of rocks and leaching of soils, dissolution of aerosol particles from the atmosphere and from several anthropogenic activities such as mining, processing and the use of metal based materials. The major and trace elements such as Ca, Mg, K, Na, Mn, Mo, Co, Fe, Cu, Cr, Se and Zn are essential nutrients for most life on earth, including humans and animals. They are essential because they form an integral part of one or more enzymes involved in a metabolic or biochemical process. High level of them are associated with an increased risk for cancer, heart disease and other illness such as endocrine problem, arthritis, diabetes and liver disease (ATSDR, 2015). The chemical composition of groundwater in the study area is shown in Table 2. The chemical composition of the groundwater is controlled by nature of geochemical reaction, velocity and volume of groundwater flow, lithology, precipitation and role of human activity (WHO, 2008).

Calcium and magnesium are abundant in rocks and soil, particularly lime stones and dolomites. They are relatively soluble and dissolve in surface water and then enter into ground water. It is a major component of the solutes in most natural water and it is an important contributor to the hardness of water. The mean concentration of calcium in groundwater samples was 61.97 mg/l. Calcium is an essential element which is important for human cell physiology and bones. It is needed for teeth, bone tissue, heart function, nerve impulses, pH regulation and contraction of muscles. The higher the calcium loss, the greater is the risk of osteoporosis, coronary artery disease, high blood pressure and a long list of degenerative diseases generally associated with premature aging (WHO, 2009). Magnesium is an essential element and the most abundant element on earth is a main constitute in minerals like dolomite, magnetite etc. It is a common constituent of natural water and it is an important contributor to the hardness of water. The mean concentration of magnesium in groundwater samples was 2.408 mg/l. It is a cofactor for many cellular enzymes, many of which are involved in energy metabolism. It is also involved in protein and nucleic acid synthesis and is needed for normal vascular tone and insulin sensitivity (WHO, 2009). Calcium and magnesium occurs in drinking water at concentrations well below those of health concern; therefore no guideline values have been established.

Potassium is an essential element in plant, animal and human nutrition. It can occur naturally in minerals and from soils. Potassium, along with sodium, is responsible for the regulation of fluids inside of the cells (ATSDR, 2015). The mean concentration of potassium in groundwater samples was 0.699 mg/l. Potassium occurs in drinking-water at concentrations well below those of health concern; therefore no guideline values have been established. Sodium is an abundant natural constituent of rocks and soils and found in less quantity in water. Sodium is an essential element necessary in the functioning of the nervous system and the brain. The high concentration of sodium impart taste to the water and make it unfit for everyday use and leads to cardiovascular diseases and high blood pressure (Terrence *at al*., 2007). Sodium was not detected in groundwater samples.

Table 2. The mean values of major and trace elements of groundwater samples in the village Pepaj, Rugova

Elements (mg/l)	Groundwater	EU (1998)	WHO (2008)	USEPA (2012)
Ca	61.97	-	-	-
Mg	2.408	-	-	-
K	0.699	-	-	-
Na	ND	200	-	-
Mn	0.006	0.05	0.04	0.05
Mo	ND	-	0.07	-
Co	ND	-	-	-
Fe	0.194	0.2	-	0.3
Zn	0.362	-	-	5.0
Se	ND	0.01	0.01	0.05
Ni	ND	0.02	0.07	-
Cu	0.028	2.0	2.0	1.3
Cr	0.008	0.05	0.05	0.1
Al	0.011	0.2	-	0.2
Sr	ND	-	-	-
Sb	ND	0.005	0.02	0.006
Ba	0.019	-	0.7	2.0
Cd	ND	0.005	0.003	0.005
As	ND	0.01	0.01	0.01
Hg	ND	0.001	0.006	0.002
Pb	ND	0.01	0.01	0

Manganese usually occurs together with iron and is widely distributed in soil, sedimentary rocks and water. Manganese is an element essential to the proper functioning of both humans and animals, as it is required for the functioning of many cellular enzymes (ATSDR, 2015). The mean value of manganese in the groundwater samples was 0.006 mg/1, which is lower than permissible standards (table 2). Health effects over uptake of manganese led to muscle weakness, sensory problems and inadequate testosterone levels. Molybdenum is an essential component of many enzymes for the proper function of important enzymes. Deficiencies occur most often in those with metabolic conditions, while excess amounts can cause poor copper retention (Strachan, 2010). Molybdenum was not detected in groundwater samples.

In nature, cobalt is frequently associated with nickel, and both are characteristic components of meteoric iron. The main ores of cobalt are cobaltite, erythrite, glaucodot and skutterudite. Cobalt is essential element and has both beneficial and harmful effects on human health. A biochemically important cobalt compound is vitamin B12 which is essential for good health in animals and humans. When too much cobalt is taken into body, however, harmful health effects can occur on the lungs, including asthma, pneumonia and wheezing (ATSDR, (2015). Cobalt was not detected in groundwater samples. Iron is essential element for good health because it transports oxygen in blood. The shortage of iron causes disease called anaemia and prolonged consumption of drinking water with high concentration of iron may lead to liver disease called as haermosiderosis (McDermid & Lönnerdal, 2012). The mean concentration of iron in groundwater samples was 0.194 mg/l, which is within the permissible limits (table 2). Besides natural sources, from rock weathering the corrosive nature of casing pipe used for water supply might contribute to the elevated iron concentration.

The most common zinc ore is sphalerite, a zinc sulphide mineral. Zinc is an essential and beneficial element in body growth. Zinc is a component of many enzymes important for immune function and with catalytic and structural roles. It is necessary for wound healing, regeneration of new cells, and acid-base balance as a component of carbonic anhydrase. Consumption of excess zinc can cause ataxia, lethargy, copper deficiency and neurological dysfunction (Underwood, 1977). The mean zinc concentration in groundwater was 0.362 mg/l which is within the limits as prescribed by US EPA standard. Selenium occurs in elevated amounts in groundwater in connection with sulphide ores and in areas with alkaline soils. Selenium is nutritionally essential for humans. It is a powerful antioxidant which works in concert with vitamin E to support the operation of antioxidant enzymes, and may reduce the risk of abnormal cell growth, as will many other antioxidants. It supports cardiovascular health and supports the thyroid and nervous system. The toxic effects of its long term exposure are manifested in liver damage (Underwood, 1977). Selenium was not detected in groundwater samples.

Copper normally occurs in drinking water through mineral dissolution and through corrosion of copper alloy water distribution pipes. Copper is an essential element, concentrated in several enzymes, and its presence in trace concentrations is essential for the formation of haemoglobin. Excessive amount of copper uptake in drinking water may lead to chronic anaemia, coronary heart diseases and high blood pressures (Strachan, 2010). The mean concentration of copper in groundwater samples was 0.028 mg/l, which is within the permissible limits (table 2). Chromium within the recommended limit in drinking water is essential in human nutrition to maintain the normal glucose metabolism. However, if higher than the recommended level, it can cause dermatitis and ulceration of the skin. Long-term exposure can cause kidney, liver, circulatory and nerve tissue damages (Strachan, 2010). The mean value of chromium in groundwater samples was 0.008 mg/l, which is lower than permissible levels (table 2).

Trace elements such as Ni, Al, Ba, Sr, Sb, Cd, As, Hg and Pb have no established biological functions and are considered as non-essential metals. The common nickel-bearing minerals include garnierite (Ni-silicate) in nickel-rich laterite, pentlandite, arnierite. Small amounts of nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Nickel was not detected in groundwater samples. Nickel compounds are carcinogenic and metallic nickel is possibly carcinogenic (ATSDR, 2015). Aluminium is the most abundant metal in the earth's crust occurring in mineral rocks and clays. In our study the mean value of aluminium in groundwater samples was 0.011 mg/l, which is lower than permissible limit (table 2). Because aluminium competes with calcium for absorption, increased amounts of dietary aluminium may contribute to the reduced skeletal mineralization (osteopenia) observed in infants with growth retardation. In very high doses, aluminium can cause neurotoxicity, and is associated with altered function of the blood-brain barrier (Thiedemann & Howe, 1997). Strontium is a naturally occurring element found in rocks, soil, dust, coal, oil and phosphate fertilizers. Strontium ore is found in nature as the minerals celestite and strontianite. Ingestion of small amounts of strontium is not harmful. However, exposure to high levels of naturally-occurring strontium during infancy and childhood can affect bone growth and cause dental changes (ATSDR, 2015). Strontium was not detected in groundwater samples. There is not a drinking water standard for strontium at this time by EU (1998), WHO (2008) and USEPA (2012).

Antimony is a metalloid element, it is naturally occurring from weathering of rocks, and in flame retardant materials. It can also occur naturally from weathering of rocks. Exposure to high levels of antimony for short periods of time causes nausea, vomiting, and diarrhea. There is little information on the effects of long-term antimony exposure, but it is a suspected human carcinogen (Terrence *at al*., 2007). Antimony was not detected in groundwater samples. Barium is not considered to be an essential element for human nutrition (Schroeder *et al*., 1972). The short-term or acute problems include increase in blood pressure, gastrointestinal problems, muscle weakness, and affects the nervous and circulatory system. It occurs in a number of compounds, most commonly barium sulphate (barite) and, to a lesser extent, barium carbonate (witherite). The mean concentration of barium in groundwater samples was 0.019 mg/l, which is within permissible standard limits (table 2).

Because of their high degree of toxicity and carcinogenicity Cd, As, Hg and Pb, rank among the priority metals that are of public health significance. Cadmium occurs naturally in zinc, lead, and copper ores which act as source to groundwater and surface waters. Cadmium was not detected in groundwater samples. Cadmium is non-essential element and in humans on long-term exposure is highly toxic. When cadmium enters the body it is accumulated in the kidneys and can cause problems such as kidney dysfunction. Brittle bones, lung cancer and acute pneumonia are other health effects that arise from cadmium exposure (Robards & Worsfold, 1991). Arsenic is a toxic non-essential element present in the drinking water, resulting from both anthropogenic and geogenic sources. High concentration of arsenic causes metabolic disorder. It also causes dermatitis and the irritation of upper respiratory passage, ulceration and perforation of nasal septum, lung cancer (ATSDR, 2015). Arsenic was not detected in groundwater samples.

Naturally occurring mercury has been widely distributed by natural processes such as volcanic activity. Mercury is a non-essential element and its compounds are toxic and exposure to excessive levels can permanently damage or fatally injure the brain and kidneys. Elemental mercury can also be absorbed through the skin and cause allergic reactions. Ingestion of inorganic mercury compounds can cause severe renal and gastrointestinal toxicity (ATSDR, 2015). Mercury was not detected in groundwater samples. The common lead-bearing minerals include galena, anglesite, boulangerite, cerussite and pyromorphite. It is the most significant of all the metals because it is toxic, very common and harmful even in small amounts. Lead is toxic to the central and peripheral nervous system causing neurological and behaviour effects. The consumption of lead in higher quantity may cause hearing loss, blood pressure and hypertension and eventually it may be prove to be fatal (Terrence *at al*., 2007). Lead was not detected in groundwater samples.

Conclusion

From the obtained results, it can be concluded that mean values of physico-chemical parameters and concentrations of major and trace chemical elements of groundwater samples were found to be within the permissible limits set by 98/83/EC Directive, WHO and US EPA standards. The most abundant anions in groundwater are bicarbonate (280 mg/1) followed by sulphate (5 mg/1), nitrate (1.53 mg/1), ammonia (0.177), chloride (0.1mg/1) and fluoride (0.09 mg/1), while phosphate were not detected. High concentration of bicarbonates in groundwater is deviated by weathering of calcium bearing rocks, such as limestone, dolomite and calcite. The mean concentrations of major and trace elements were: Ca (61.97 mg/l), Mg (2.408 mg/l), K (0.699 mg/l), Mn (0.006 mg/l), Fe (0.194 mg/l), Zn (0.362 mg/l), Cu (0.028 mg/l), Cr (0.008 mg/l), Al (0.011 mg/l) and Ba (0.019 mg/l). While Na, Mo, Co, Se, Ni, Sr, Sb, Cd, As, Hg and Pb were not detected. The concentrations of all elements have natural origin connected to geology of study area. The high concentration of Ca in groundwater samples originate from geologic formation, deviated by weathering of calcium bearing rocks. The water is hard due to the presence of calcium and magnesium in the aquifers. The findings revealed that the quality of groundwater is excellent for drinking purposes, it is pure, unpolluted and rich with major and trace elements that that influence the flavour and good health.

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