Assessment of Major and Trace Elements of Fresh Water Springs in Village Pepaj, Rugova Region, Kosova

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Abstract: Water is essential to health however its purity and the mineral content are important for consumption by humans. In recent years, there has been an increasing global public health concern associated with drinking water contamination by major and trace chemical elements. In mountain Rugova Region the natural springs are the most important source of water for drinking and domestic uses. The aim of this study was to assess the major and trace elements of spring waters in the village Pepaj, Rugova. Springs waters were analysed for their major and trace elements in order to assess their water quality. The concentrations of major and trace elements were determined by Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES). All results were compared with the drinking water standards of the EU (98/83/EC Directive), World Health Organization and US Environmental Protection Agency. While concentrations of Ca, Mg, K, Mn, Mo, Fe, Zn, Ni, Cu, Cr, Al and Ba were within the permissible limit values, Na, Co, Se, Sr, Sb, Cd, As, Hg and Pb were not detected in waters of springs. The highest concentrations of Ca, Mg, K, Mn, Mo, Fe, Zn, Ni, Cu, Cr, Al and Ba were 67.96 mg/l, 1.242 mg/l, 0.912 mg/l, 0.037 mg/l, 0.001 mg/l, 0.192 mg/l, 0.885 mg/l, 0.011 mg/l, 0.032 mg/l, 0.015 mg/l, 0.0239 mg/l and 0.0174 mg/l, respectively. The findings revealed that there were no public health risk in view of major and trace elements concentration in waters of springs.

Keywords: Rugova Mountain Region, spring water, major and trace elements, drinking water quality, (ICP-OES)

Introduction

Springs are the most important source of water used for domestic and other purpose in Rugova Region. The ecology of cold springs differs markedly from that of other aquatic environments, because the springs provide cold and clear water. Natural springs occur where groundwater emerges from rock stratum containing an aquifer. In contrast to surface water, groundwater is usually of higher water quality. Few manifestations of groundwater have yielded more interest than springs. In this context, springs were largely responsible for determining the sites of ancient settlements (Meuli & Wehrle, 2001). Nowadays, modern techniques allow the construction of deep drilled wells. Yet, springs are still an important groundwater source since they are easily accessible and usually provide clean drinking water. Conditions necessary to produce springs are many and are related to different combinations of geologic, hydrologic, hydraulic, climatic and even biologic controls (Eftimi, 2005).

Quality of spring waters is influenced by several factors as climate, kind of subsoil within which water flows, time of contact water-carbonate rock, characteristics and utilization of the ground. Springs water chemistry to a large extent, is influenced by elemental distribution often determined by the, geology, chemical composition of the underlying rocks, lithologic effects, climate, groundwater flow and anthropogenic activities. Although major and trace elements in water are naturally occurring elements that are found throughout the earth’s crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, industrial production, agricultural, domestic effluents and atmospheric sources (He et al., 2005).

Though water of springs has been considered to be pure because of its filtration through layers of soil and rocks it has its own health and acceptability problems based on concentration level of certain chemical elements. There are many major and trace elements derived from natural dissolved mineral in water. The iron, zinc, copper, manganese, magnesium, molybdenum, cobalt and selenium are

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essential nutrients but excessive concentrations would cause risk for human health. Same trace elements such as cadmium, arsenic, mercury, and lead do not have beneficial effects in humans and are toxic (Goyer et al., 2001). Therefore the aim of this study was to assess concentration of major and trace elements of fresh water springs in village Pepaj, Rugova Region.

Materials and Methods

General description of sampling site
Water samples were collected from natural springs in village Pepaj, Rugova. 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 springs surveyed are chosen according to the frequency of use by residents. They are located at geographical coordinates and elevation identified by using global positioning system (GARMIN GPS map 62). The name and coordinates of springs studied are summarized in table 1. Figure 1 shows the topography and location of springs in the study area, village Pepaj.

Table 1. Name and geographical coordinates of springs studied in village Pepaj, Rugova

<table>
<thead>
<tr>
<th>Code</th>
<th>Spring name</th>
<th>Geographical coordinate</th>
<th>Elevation (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Pusi ne Pllana</td>
<td>X-7428394 : Y-4732916</td>
<td>1691</td>
</tr>
<tr>
<td>S2</td>
<td>Gurra e leprit</td>
<td>X-7428549 : Y-4732703</td>
<td>1636</td>
</tr>
<tr>
<td>S3</td>
<td>Gurra e kryse</td>
<td>X-7428434 : Y-4732476</td>
<td>1574</td>
</tr>
</tbody>
</table>

Figure 1. Map depicts topography and location of the springs 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 formations. 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 (Antonjievic 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 major and trace elements analysis**

The samples of water were collected from springs in village Pepaj during October 2016 for major and trace chemical elements examinations. They were collected in high-density polyethylene bottles of one litre capacity. Prior to collection, the bottles were washed with distilled water and subsequently rinsed thoroughly with the sample water. Samples from the springs S2 and S3 were taken direct form springs outlet while the samples from spring S1 were taken from waterhole collected direct from spring. For validation of results, three water samples were collected at every site of sampling. Collected samples were immediately acidified in the field to pH <2.0 by adding HNO3. In meantime the collected samples were stored in cool box and transported to N.SH. Agrovet Laboratory, Pristhina. Water samples were preserved according to standard procedures (APHA, 2005). The concentrations of major and trace elements such as Ca, Mg, Na, K, Al, As, Ba, Fe, Mn, Cd, Co, Cr, Cu, Ni, Zn, Pb, Sb, Sr, Se, Hg and Mo were determined 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.

**Result and Discussion**

The results of the major and trace elements analysis of water samples collected from springs in village Pepaj are summarized in table 2. Water samples collected from these spring sources have crystal clear appearances, a good taste and were odourless. The obtained results were compared with maximum values recommended by EU (98/83/EC Directive, 1998), WHO (2008) and US EPA (2012) drinking water standards. The major and trace elements such as Ca, Mg, K, Na, Mn, Mo, Co, Fe, Cu, Cr, Se and Zn are essential nutrients that are required for various biochemical and physiological functions in humans. Inadequate supply of these macro- and micro-nutrients results in a variety of deficiency diseases. They are important constituents of several key enzymes and play important roles in various oxidation-reduction reactions. Essential elements are required for biological function; however, an excess amount of such elements produces cellular and tissue damage leading to a variety of adverse effects and human diseases. For some including chromium and copper, there is a very narrow range of concentrations between beneficial and toxic effects. Other elements such as Ni, Al, Ba, Sr, Sb, Cd, As, Hg and Pb have no established biological functions and are considered as non-essential elements (Chang et al., 1996). 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.

Potassium is derived from silicate minerals like orthoclase, microcline, nepheline, leucite and biotite. It occurs widely in the environment, including all natural waters. Potassium is an essential element for human nutrition. It is a cofactor for many enzymes and is required for the secretion of insulin, creatinine phosphorylation, carbohydrate metabolism and protein synthesis. It is vital for human body functions like heart protection, regulation of blood pressure, protein dissolution, muscle
contraction, nerve stimulus (Sunde, 2012). Potassium concentrations in water samples collected from the springs studied varied from 0.542 mg/l at spring (S1) to 0.912 mg/l at spring (S2). Reason for not establishing a guideline value for potassium is because it occurs in drinking water at concentrations well below those of health concern.

Sodium occurs in minerals including halite (sodium chloride) amphibole, zeolite and cryolite. Sodium is an essential element necessary in the functioning of the nervous system and the brain. Sodium, along with potassium, is responsible for the regulation of fluids inside of the cells. Excessive intake can cause hypertension but the primary mode of intake is via food. High blood pressure can increase the risk of heart attack, stroke, or kidney disease (WHO/FAO/IAEA, 1996). Sodium in the study area was not detected in any of the analysed samples from springs.

Table 2. Results of major and trace elements concentrations of waters from springs in the village Pepaj, Rugova

<table>
<thead>
<tr>
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<tbody>
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<td>55.43</td>
<td>65.70</td>
<td>-</td>
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<tr>
<td>Mg</td>
<td>1.242</td>
<td>1.214</td>
<td>0.923</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>0.542</td>
<td>0.912</td>
<td>0.755</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>0.007</td>
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<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
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<tr>
<td>Mo</td>
<td>0.001</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
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<td>-</td>
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<tr>
<td>Fe</td>
<td>0.189</td>
<td>0.192</td>
<td>0.153</td>
<td>0.2</td>
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<tr>
<td>Zn</td>
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<td>0.689</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Se</td>
<td>ND</td>
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<tr>
<td>Ni</td>
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<td>ND</td>
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<td>0.028</td>
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<td>Cr</td>
<td>0.003</td>
<td>0.015</td>
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<td>0.0166</td>
<td>0.2</td>
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<tr>
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<td>ND</td>
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<td>ND</td>
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<td>-</td>
</tr>
<tr>
<td>Sb</td>
<td>ND</td>
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<td>ND</td>
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<td>0.02</td>
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<tr>
<td>Ba</td>
<td>0.0174</td>
<td>0.0028</td>
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<tr>
<td>Cd</td>
<td>ND</td>
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<td>ND</td>
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<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>As</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.01</td>
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</tr>
<tr>
<td>Hg</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.001</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>Pb</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.01</td>
<td>0.01</td>
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</tr>
</tbody>
</table>

Calcium is the most abundant of the alkaline-earth metals and is a main constituent of lime stones and dolomites. The most general forms of calcium in sedimentary rocks are carbonates. They are relatively soluble and dissolve in water. Calcium is an essential element for all forms of life and is a major component of the solutes in most natural water. The water from spring S1 has the highest level of Ca (67.96 mg/l), while water from spring S2 has the lowest value of Ca (55.43 mg/l) as shown in figure 2a. The higher calcium concentrations from these springs can be the consequence of higher layer of underground accumulation of these waters. In its way towards the spring, water from these springs has higher contact with minerals of calcium and magnesium. Higher concentration of calcium in spring waters is an important contributor to the hardness of water (Lajić et al., 2016). Calcium plays important roles in bone structure, heart function, muscle contraction, nerve impulse transmission and blood clotting, while calcium deficiency can cause osteoporosis (WHO, 2009). There are no health concerns associated with calcium and magnesium, but the water containing these elements may contribute towards human dietary needs, however, their high concentration may cause scaling of pipes.

Magnesium may be derived from dissolution of magnesium calcite, gypsum and dolomite from source rocks. Magnesium is an essential element for proper functioning of living organisms. It is a
common constituent of natural water and it is an important contributor to the hardness of water. It is included in many different enzyme reactions, and is important for the carbohydrate metabolism, heart, muscles, nerve impulses and the activation of enzymes to metabolize blood sugars. It is also vital for proper bone growth and necessary for adequate calcium absorption (WHO, 2009). The range of magnesium concentrations in water of the springs was from 0.923 mg/l (S3) to 1.242 mg/l (S3) as shown in figure 2b. Magnesium usually occurs in smaller concentration in water than calcium because the dissolution of magnesium rich minerals is a slow process.

Figure 2. Variations of Ca (a) and Mg concentrations (b) from various spring’s water

Manganese is one of the most abundant metals in the earth’s crust, usually occurring with iron. The most abundant compounds of manganese are sulphide, oxide, carbonate and silicate. It occurs naturally in many surface water and groundwater sources. Manganese is an essential element for many living organisms, including humans. Highest concentration of manganese was observed in the samples from spring S3 (0.037 mg/l) while lowest concentration was found in the samples from spring S1 (0.007 mg/l). The concentrations of manganese in all samples were below the permissible limits (table 2). Manganese is critical to the metabolism of bones, and is essential for enzyme reactions, and healthy brain thyroid and nervous systems. Health effects over uptake of manganese led to muscle weakness, sensory problems and inadequate testosterone levels (Strachan, 2010).

Molybdenum is an essential element and a cofactor for various enzymes involved in hydroxylation reactions, including aldehyde oxidase, xanthine oxidase/dehydrogenase and sulphide oxidase. There is no well-described deficiency syndrome although seizures and psychiatric phenomena may occur. Molybdenum toxicity causes a physiological copper deficiency (Strachan, 2010). The concentrations of molybdenum in waters of springs ranged from under detected limit (S2 and S3) to 0.001 mg/l (S1). The concentration of Mo in the study area was below the permissible limits (table 2).

Cobalt in compound form occurs as a minor component of copper and nickel minerals. Cobalt may enter the environment from both natural sources and human activities. It may enter air and water, and settle on land from windblown dust, seawater spray, volcanic eruptions, and forest fires and may additionally get into surface water from runoff and leaching when rainwater washes through soil and rock containing cobalt. In all analysed samples from springs cobalt was not detected. Cobalt is essential element and has both beneficial and harmful effects on human health. It is beneficial for humans because it is part of vitamin B12, which is essential to maintain human health. When too much cobalt is taken into body, however, harmful health effects can occur on the lungs, including asthma, pneumonia, and wheezing (Yamada, 2013).

Due to its high abundance within the earth crust, iron is ubiquitous in all fresh water environments and often reaches significantly higher concentrations in water than trace metals. Iron is an essential element in human nutrition. It has an essential role as a constituent of enzymes such as cytochromes and catalase, and of oxygen transporting proteins such as hemoglobin and myoglobin (McDermid & Lönnerdal, 2012). Deficiency of iron results in hyochromic macrobiotic anemia, one of the world’s common health problems. Long-time consumption of drinking water with a high concentration of iron can lead to liver diseases (hemosiderosis). The highest concentration of iron (0.192 mg /l) was observed in the samples from spring S2 while lowest concentration of iron was
found in the samples from spring S3 (0.153 mg/l) as shown in figure 3a. The concentrations of iron in all analysed samples from springs were below the permissible limits (table 2).

![Fe, mg/l](image1) ![Zn, mg/l](image2)

**Figure 3.** Variations of Fe (a) and Zn concentrations (b) from various spring’s water

The principal zinc ores are sulphides, such as sphalerite and wurzite. Zinc is an essential trace element which functions as catalyst for enzymatic activity in human bodies. It is required to support the immune system, protein synthesis, and reproductive health. But high levels of zinc may cause adverse health effects like anaemia and injury to the pancreas and kidney, disturb protein metabolism and cause arteriosclerosis. Zinc deficiency results in poor wound healing, reduced work capacity of respiratory muscles, immune dysfunction, anorexia, diarrhoea, dermatitis and depression (Elinder, 1986). Higher concentration of zinc was observed in the samples from spring S1 (0.885 mg/l) while lowest concentration was found in the samples from spring S2 (0.325 mg/l) as shown in figure 3b. The differences in zinc concentrations in water of springs are specific to hydrogeology and hydrochemistry of the sampling points. In all analysed samples zinc concentrations were below the permissible limits (table 2).

Selenium occurs in elevated amounts in groundwater in connection with sulphide ores and in areas with alkaline soils. Selenium is nutritionally essential element for humans. It is incorporated into proteins to make selenoproteins, which are important antioxidant enzymes that play critical roles in reproduction, thyroid hormone metabolism and protection from oxidative damage and infection (Sunde, 2012). Selenium toxicity is similar to arsenic poisoning and causes abdominal pain, nausea and vomiting, irritability, parasthesia, and hyper-reflexia. In study area selenium was not detected in any of the analysed samples from springs.

The common nickel bearing minerals include garnierite (Ni-silicate) in nickel-rich laterite, pentlandite, arnietite. In groundwater, nickel can be present through the weathering of rocks and as a result of human activities, such as the burning of fossil fuels, smelting, and the electroplating industry. Nickel has not been shown to be an essential nutrient for humans, but it may serve as a cofactor or structural component of specific metalloenzymes with a variety of physiologic functions. Nickel facilitates ferric iron absorption or metabolism. Although nickel may be toxic in high concentrations, the concentrations in water are not usually high enough to cause health concerns (WHO/FAO/IAEA, 1996). The concentration of nickel in waters of springs ranged from under detected limit (S1 and S3) to 0.011 mg/l at spring S2, which is lower than permissible levels (table 2).

Copper is found mainly as a sulphide, oxide, or carbonate in the minerals. Copper enters the water through mineral dissolution, industrial effluents and through corrosion of copper alloy water distribution pipes. Copper is an essential component of many enzymes and a coenzyme. Its presence in trace concentrations is essential for the formation of haemoglobin, wound healing and immune function (Sunde, 2012). The highest concentration of Cu was detected in the sample from spring S2 (0.032 mg/l) while the lowest concentration of Cu was detected in the sample from spring S1 (0.024 mg/l) as shown in figure 4a. The present study indicated that overall Cu level in the study area were lower than permissible levels (table 2). It is a potential health hazard that causes various health problems when people are exposed to it at levels above the permissible value. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting while use of water
whose copper level exceeds the maximum value over many years causes liver or kidney damage (Sunde, 2012).

![Graphs showing variations of Cu and Cr from various spring's water](image)

**Figure 4.** Variations of Cu (a) and Cr (b) from various spring’s water

Chromium is essential element to several enzyme systems, including that which works with insulin in the processing of glucose. Chromium deficiency has been shown to be linked to blood sugar imbalance and improper metabolism. Chromium in excess amounts can be toxic especially in the hexavalent form. Ingestion of chromium in large amounts can cause stomach upsets and ulcers, convulsion, kidney and liver damage and even death (Strachan, 2010). The highest concentration of Cr (0.015 mg/l) was detected in the samples from spring S2 while the lowest concentration of Cr (0.002 mg/l) was detected in the samples from spring S3 as shown in figure 4b. The present work indicated that overall chromium level in the study area were lower than permissible levels (table 2).

Aluminium is the most abundant element found in the earth crust in mineral rocks and clays, but it is found in trace amount in natural waters. Aluminium is non-essential element, it is considered to be less toxic. 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 (ATSDR, 2015). In our study, spring waters have aluminium concentration of 0.0160 (S1), 0.0239 (S2) and 0.0166 mg/l (S3), respectively. The concentration of aluminium in all the water samples were below the standard limits (table 2).

Strontium is non-essential element that is found naturally in the minerals celestine and strontianite. Strontium occurrence is also linked to anthropogenic sources such as air contamination from milling processes, coal burning, and phosphate fertilizers. Naturally occurring strontium is released into fresh water from geologic weathering. There are no harmful effects of stable strontium in humans at the levels typically found in the environment. As a molecular surrogate for calcium, strontium has been administered to osteoporosis patients at low doses over several years along with calcium and vitamin D with no adverse side-effects (ATSDR, 2015). Strontium has the greater potential to accumulate in the bones of children than in adults because of the high calcium requirement during the developmental stages of life. Strontium was not detected in any of the analysed samples.

Antimony is non-essential element, it is naturally occurring from weathering of rocks, but the most common source of antimony in drinking water is the corrosion of antimony containing plumbing materials. 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. Most antimony compounds do not bioaccumulate in aquatic life (WHO, 2003). In analysed water samples from springs antimony was not detected.

Barium is not considered to be an essential element for human nutrition. The short-term or acute problems include increase in blood pressure, gastrointestinal problems, muscle weakness, and affects the nervous and circulatory system. Barium is generally present in air in particulate form as a result of industrial emissions particularly from combustion of coal and diesel oil. It occurs in a number of compounds, most commonly barium sulphate (barite) and, to a lesser extent, barium carbonate.
(witherite). Barium could be derived from the weathering of minerals such as barite and witherite (Schroeder et al., 1972). The higher concentration of barium was found in spring water S1 (0.0174 mg/l) while the lower concentration was found in spring water S2 (0.0028 mg/l). All the spring waters samples have barium concentrations below the permissible standard limits (table 2).

Cadmium occurs naturally in zinc, lead and copper ores which act as source to ground and surface waters. Cadmium concentrations in unpolluted natural waters are usually minimal. Elevated cadmium levels in water have also been associated with runoff from agricultural land where fertilisers are used but the springs water catchment areas in the present study did not have these types of land uses. Cadmium was not detected in any of the analysed water samples from springs. Cadmium is a toxic non-essential element and responsible for several cases of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures, kidney damage, etc. (Rajeswari & Namburu, 2014).

Arsenic is non-essential element and one of the major carcinogenic pollutants present in water resulting from both geogenic and anthropogenic sources. Arsenic occurs naturally in the earth’s crust, with higher concentrations in some geographic areas, and in some types of rocks and minerals. It is introduced into drinking water through the dissolution of naturally occurring minerals and ores. The presence of high to very high levels of arsenic does not modify the taste, colour or odour of water. Consumption of elevated levels of arsenic through drinking water is related to the development of cancer at several sites, particularly skin, bladder and lung (ATSDR, 2015). In all analysed samples from springs arsenic was not detected.

Natural sources of mercury include volcanoes, forest fires, cannabar (mercury sulphide) and fossil fuels such as coal and petroleum. Anthropogenic sources of mercury in the environment include incinerators, coal-burning facilities, etc. Mercury was not detected in any of the analysed samples. Mercury is a toxic non-essential element which has no known function in human biochemistry or physiology. The toxic effects of inorganic mercury compounds are seen mainly in the kidney following short and long-term exposure. In humans, acute oral poisoning results primarily in haemorrhagic gastritis and colitis and kidney damage (WHO, 2005).

The common lead bearing minerals include galena, anglesite, boulangerite, cerussite and pyromorphite. Lead is a toxic non-essential element that is harmful to human health; there is no safe level for lead exposure. It causes neurological disorders, reproductive problems, damages kidneys, anaemia and diminished intelligence. Lead toxicity occurs because it mimics many aspects of the metabolic behavior of calcium and inhibits many enzyme systems. High levels of lead contamination in a child can result in convulsions, major neurological damage, organ failure, coma and ultimately death. Unlike other contaminants, lead will accumulate within the body over time, i.e., bioaccumulate (ATSDR, 2015). Lead was not detected in any of the analysed water samples from springs.

Conclusion
From the obtained results, it can be concluded that the concentrations of major and trace chemical elements in water samples from springs such as Ca, Mg, K, Mn, Mo, Fe, Zn, Ni, Cu, Cr, Al and Ba were found to be within the permissible limits set by 98/83/EC Directive, WHO and USEPA standards. However, the concentrations of Na, Co, Se, Sr, Sb, Cd, As, Hg and Pb were not detected in any samples of springs. The concentration of major and trace elements in the springs samples were found within the following range Ca (55.43-67.96 mg/l), Mg (0.923-1.242 mg/l), K (0.542-0.912 mg/l), Mn (0.007-0.037 mg/l), Mo (ND-0.001 mg/l), Fe (0.153-0.192 mg/l), Zn (0.325-0.885 mg/l), Ni (ND-0.011 mg/l), Cu (0.024-0.032 mg/l), Cr (0.002-0.015 mg/l), Al (0.016-0.0239 mg/l) and Ba (0.0028-0.0174 mg/l). A high concentration of Ca in spring waters is deviated by weathering of calcium bearing rocks. The concentration of major and trace elements in the spring samples show some variations according to sampling areas. The spring water S1 has the higher concentration of Ca, Mg, Ba, Cr and Zn than springs S2 and S3. While the springs water S2 has the higher concentration of K, Al, Fe, and Cu than the spring S1 and S3. The differences in major and trace elements concentrations in water of springs are related to the hydrogeology and hydrochemistry of the sampling points. The concentrations of all elements have natural origin connected to geology of study area. The study reveals that the water of springs in the study area is pure, unpolluted and rich with major and trace elements that influence the flavour and good health.
References
US EPA Method 3015 (1994) Microwave Assisted Acid Digestion of Aqueous Samples and Extracts.