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The occurrence and evolution of arsenic in aquifers of the Avala volcanic complex (outskirts of Belgrade, Serbia)

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Abstract. Avala Mountain is accommodated 15 km southward from the city of Belgrade and extends over the area of about 10 km^2. Avala Mountain is a cultural and historical heritage of Belgrade qualified by the Law on Environmental protection. The area is abundant with water springs that have been exploited by tourist facilities and local population. By analyzing groundwater sampled from several springs and wells located in a vicinity of the Avala magmatic entity here we study the occurrence, concentration and origin of arsenic pollutant. The investigated springs are accommodated within the faulted complex of Mesozoic carbonate and clastic sediments, serpentinite, further intruded by the Tertiary magmatic rocks. By using the concentrations of the major and minor components(e.g. Cr, Ni, Fe, Mn) in groundwater, the relationship between groundwater and local lithostratigraphic units is outlined.
Chemical analysis of the investigated waters shows that arsenic concentration in groundwater of the investigated area is in range from 3.0 to 102.0 μg/l. Arsenic concentrations over the maximum allowed value in drinking water (10 μg/l) are detected in more than 55% cases. The occurrence of arsenic in groundwater can be attributed to local igneous rocks, i.e. to the process of oxidation of sulphide minerals with As (major or minor presence) – primarily arsenopyrite or pyrite. Groundwater with higher concentration of arsenic (above10 μg/l) is exploited as drinking water used by tourists and by local population. Along term use of the water with high concentration of arsenic impose a major health risk.

Key words:
arsenic, groundwater aquifer, volcanic complex, Avala.

Апстракт. Планина Авала смештена је 15 km јужно од Београда и простире се на површини од око 10 km^2. На том простору се налазе неки од каптираних извора и бунара из којих воду употребљавају туристи и локално становништво. У овом раду анализирана је појава, концентрација и порекло арсена у подземној води аквифера вулканског комплекса Авале. Њега чини испуцали мезозојски офиолитски комлекс додатно испресецан терцијарним магматитима. Корелације између главних компонената (катјона и анјона), као и микрокомпонената (као што су Cr, Zn, Ni, Fe, Mn и As) указала је на могућу везу између подземне воде и литостратиграфских јединица. Хемијском анализом утврђено је да је опсег концентрација As од 3.0–102.0 μg/l. Максимална довољена концентрација (10 μg/l) премашена је у 55% испитиваних узорака.

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Присуство арсена у испитиваним узорцима може бити пореклом из локалних магматских стена, односно последица оксидације минерала у којима је As главна или споредна компонента (арсенопирит и пирит), чије је присуство доказано у испитиваној области. Дуготрајном свакодневном употребом подземне воде у којој је доказано присуство As у концентрацијама изнад 10 μg/l може представљати висок ризик по здравље.

Кључне речи:
арсен, подземна вода, аквифер вулканског комплекса, Авала.

Introduction

Arsenic is a chemical halcophile and siderophile element which occupies 20th place in the abundance in the Earth's crust, being 14th in seawater and 12th in human body. The concentration of As in unpolluted fresh waters typically ranges from 1–10 μg/l, rising to 100–5000 μg/l in areas of sulfide mineralization and mining (Mandal & Suzuki, 2002). With the beginning of the 20th century its concentration becomes a very important topic, accounting its toxicity and carcinogenicity. Namely, a long term exposure and consummation of waters with the concentrations ranging > 50 μg/l could be related to skin cancer mortality (Guo et al., 2009). For this reason, most countries have reduced maximum allowed concentrations (MAC) in drinking water by decreasing the recommended value of WHO (1999) from 50 μg/l to 10 μg/l (Pfeifer et al., 2002).

In nature arsenic constitutes many of Earth minerals occurring either as a dominant or secondary element. As a chalcophile element, arsenic occurs in the form of sulphides, arsenides and sulpharsenides of heavy metals. Arsenic also can occur in the form of oxides (arsenolite - As_2O_3), prevalent in oxidizing zones sulfide-arsenide ore. As a siderophile element, arsenic appears in the form of arsenopyrite and sulfides of iron (pyrite, marcasite).

The origin of arsenic in groundwater can be natural (geological structure, volcanism, erosion) but also may originate from anthropogenic source (utilization of herbicides, pesticides, fungicides, fossil fuels, mining, etc., Ren et al., 2007). Arsenic is redox-sensitive element and its presence, distribution, form and mobility in groundwater is the result of a complex interaction of the several geochemical parameters. These parameters include pH, Eh values, presence and distribution of other elements, organic matter and microbiological activity in water and soil (Petruševski, 2005).

At moderate or high redox potentials As occurs as a series of pentavalent (arsenate) oxyanions. However, under most reducing (acid and mildly alkaline) conditions and lower redox potential the trivalent arsenite species (AsO_3^{3-}) predominate (Mandal & Suzuki, 2002; Baringer & Reilly, 2012). In negative ion forms As adsorbs at positive-charged surface (e.g. amorphous or crystal forms of Fe, Mn oxides) (Luxton et al., 2008; Guo et al., 2009) and thus can be removed from aquatic systems.

Generally, occurrence of a higher content of As in groundwater is documented in specific geological areas/conditions: in the areas of sulfide mineralization, geothermal areas, anaerobic aquifers, in arid and semiarid areas with elevated pH values. In global scale, high concentration of arsenic in groundwater considers as the major environmental issue. In South Asia (India, Bangladesh, China, Vietnam, Taiwan), concentration reaches up to 3400 μg/l, whereas South America has documented considerably lower values 300 μg/l (Chile, Argentina) (Smedley, 2006).

A cluster of earlier investigations (e.g., Bjelić et al., 2006; Jovanić & Stanić, 2006; Dalmacia et al., 2009; Petrović et al., 2012) indicate that groundwater of Serbia have rather a scattered irregular pattern of arsenic concentration. A special attention in the number of studies is reflecting onto the occurrence of arsenic in groundwater of Vojvodina (sedimentary) aquifers of Banat and Bačka administrative areas. Another source of arsenic in Serbia could be associated with the areas of considerable geothermal potential, such as Lukovska banja spa, Jošanička banja spa, Bujanovačka banja spa. These spas are characterized by documented moderately high concentrations of arsenic (Petrović-Pantić & Zlokolica-Mandić, 2012).

The presence of arsenic within the investigated area was detected earlier, documented in several water springs of Avala Mountain (springs “Sakinac”, “Velika česma” and “Vranovac”; Fig. 1). The measured concentrations of arsenic exceed the limit of maximum allowed concentrations (MAC) of arsenic in water, according to both, the domestic and foreign regulations (10 µg/l) (Poznanović & Popović, 2009). In this study, the concentration fluctuations of As were observed during the period May–September 2008. The results of the observations suggested that there are almost insignificant variations in the measured concentrations. Therefore, a possible dilution due to the mixing of infiltrated atmospheric waters in the short time has no effect on arsenic concentrations. In order to determine the oxidation state of arsenic of this groundwater, the samples were analyzed by stripping voltammetry (Poznanović et al., 2009). The analysis corroborated that a dominant form of arsenic is As (V) (90–98% concentration of the total arsenic). The overall goal of this research is to provide a continuity of investigations depicting the distribution of the arsenic concentration in groundwater of available wells and springs; and to b) investigate the geological factors for the origin of the arsenic occurrence in ground water of aquifer of the Avala Mountain volcanic complex.

Regional geological and hydrogeological setting

The Avala magmatic and sedimentary system is a complex geological-geochemical entity with distinctive uplifted morphostructure (Fig. 1). The Avala complex represents a mixture of different Mesozoic and Cenozoic paleoenvironmental conditions characterized by different processes that yield a variety of rocks with a different geochemical imprint (Ivković et al., 1971).

A geological entity of mountain Avala comprises a complex of Mesozoic volcano-sedimentary system unconformably overlain by the highly complex of Miocene and Quaternary sequences (Fig. 1). The Mesozoic agglomeration is a product of Late Mesozoic-Tertiary magmatic activity associated with the developing and closure of ancient Vardar Ocean (NW Neotethys). The investigated area belongs to a, so-called, “Europe sub-basin” (Toljić et al., 2018). In the tectonic sense, the investigated segment is actually accommodated within the East Vardar Zone (Spahić & Gaudenyi, 2019) or the segment of the “Sava Zone” (Marović et al., 2007; Schmid et al., 2008). The oldest rock system outcropping is represented by the ophiolite-bearing system of Jurassic serpentinites (Toljić, 1995; Toljić et al., 2018) scattered over the eastern and southern section of this lower-latitude mountain (Fig. 1). The exposed oceanic lithosphere of the Avala Mt. system is stratigraphically succeeded by the interchange of deep-water flysch-like marine conditions of Lower Cretaceous age. This sequence is succeeded by another, this time dominant flysch-bearing systems of Upper Cretaceous–Paleogene age (Toljić et al., 2018). This pre-Tertiary Neotethyan tectonomagmatic agglomeration is penetrated by numerous hydrothermally altered magmatic intrusions of Late Eocene–Early Miocene age (Cvetković et al., 2004).

After the termination of magmatic activity and complete closure of this western segment of Neotethys ocean, the onset of a new extensional phase during Early Miocene resulted in continental-lacustrine system of Lower Miocene (Rundić et al., 2019). Early Sarmatian resulted in a sea water influx and new transgressional stage (Upper Miocene). The former pre-Neogene paleorelief of displaced Avala Cretaceous magmatic ophiolite-bearing entity including newly developed local ancient paleo-valleys were overlaid by a well-developed Neogene sedimentary (marine) veneer. This new sea-water ingression and associated depositional system “sealed” numerous magmatic intrusions exposed previously to erosion. The Middle Miocene marine and marine-brackish sediments are well developed and represented by a sequence of conglomerates, sandstones and limestone (Toljić, 1995; Rundić et al., 2019). The post-rift subsidence stage (Middle to Upper Miocene) was likely affected by the uplifting of the entire Pannonian basin system, closed and inverted which is marked by the onset of Quaternary deposition. Ever since the Quaternary stage, the in-

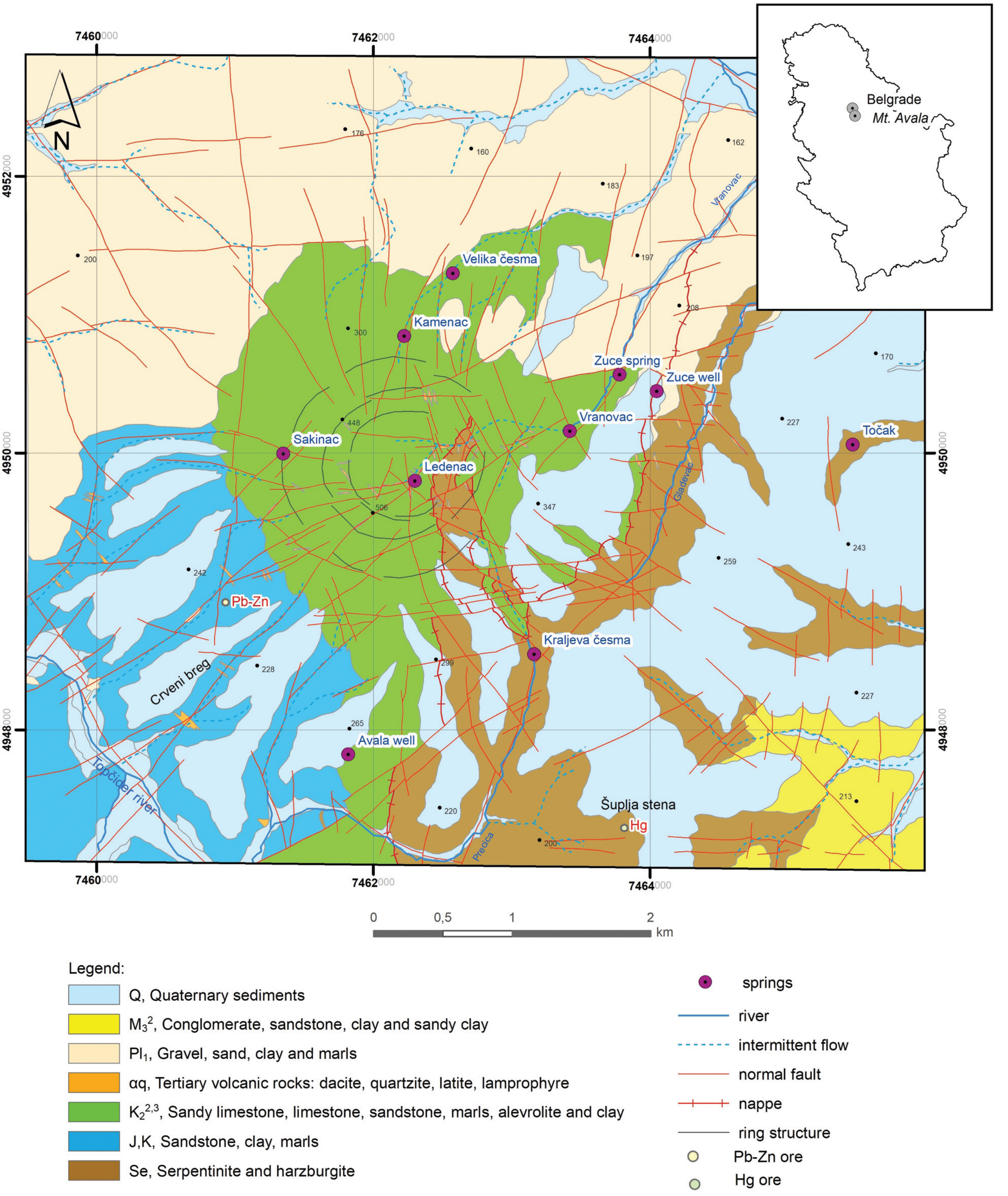

Fig. 1. *Simplified geological map of studied area (modified after Toljić, 1995) with the sampling localities.*

vestigated area underwent the exposure to terrestrial conditions (land). The post-Miocene geomorphological processes have shaped the mountain Avala and its immediate surrounding.

In contrast to a subdued surrounding, the hypsometry and a cone shape of the mountain Avala clearly (511 m) protrudes this geomorphological entity (uplifted morphostructure). Numerous inherited brittle (normal) faults are radially distributed across the investigated cone-shaped magmatic and sedimentary complex (Toljić, 1995; Fig. 1). As the extensional fault system is penetrated by a dominant set of sub-vertically emplaced intrusions of quartzlatite with basaltic and dacitic content (Fig. 1), it is to expect that a relatively large segment of the investigated magmatic entity is buried underneath a lower structural level of the Avala complex.

The average arsenic content in magmatic rocks in Serbia - andesite, dacite, quartzlatite is estimated to reach 2.6 ppm (Dangić & Dangić, 2007). However, during generation of hydrothermal sulfide ore deposits, arsenic in water-rock interaction becomes mobile and appears to be dispersed into the surrounding rocks. As a product of progressive multiphase hydrothermal activity this altered areas contain minerals enriched with arsenic (Dangić & Dangić, 2007). Commonly, during the formation of hydrothermal lead and zinc deposits, arsenic concentrates and deposits in the form of arsenopyrite, and other sulphides of arsenic, arsenides of Ni and Co, sulfarsenides Cu, Ag, Pb. Hydrothermally altered rocks are indentified across the investigated area, encircling dominantly the exposed magmatic intrusions. The prominent examples of the hydrothermal activity are observed at the Crveni breg, Prečica (southwestern mountainside of Avala), the areas of lead-zinc mineralization. Another example is the Šuplja stena area (Fig. 1), accommodated in the southeastern part of Avala-the area of Hg mineralization (cinnabar). The first example was formed in sandstone, marl and limestone of Jurassic and Lower Cretaceous age, in which are embedded the veins of quartzlatite, dacite and andesite. The ore deposits Šuplja stena appear in the zones of hydrothermally altered serpentinite, which are partly silicified and dolomitizated. The impregnations of cinnabar are accompanied with iron- sulfide ore minerals and are associated with the fracture zones trending East-West (Toljić, 1995).

In this particular area are recognized numerous minerals such as: sphalerite (ZnS), pyrite (FeS_2), pyrrhotite (FeS), arsenopyrite ($FeAsO_4$), chalcopyrite ($CuFeS_2$), galena (PbS), marcasite (FeS_2) as well as chalcocite(CuS_2), covellite (CuS) accompanied by quartz (SiO_2), calcite ($CaCO_3$), boulangerite ($Pb_5Sb_4S_{11}$), etc. (Toljić, 1995). The summary of the investigated minerals at the area of Avala and the surrounding, implicates that the main mineral of arsenic is arsenopyrite. Janezić & Tančić (2003) analyzed by X-ray diffraction method a sample of arsenopyrite associated with pyrite (collected from the vicinity of Crveni Breg mine). The authors confirmed that the formation of minerals from this area occurred under hypothermal conditions.

Hydrogeological setting

As mentioned earlier, the Avala Mountain system geomorphologically differs from its rather subdued surrounding. Interestingly, the position of water-permeable tectonic discontinuities crosscutting Avala Mt. has differences relative to the both, regional drainage system (Topčiderska and Zavojnička rivers) and the local drainage system (includes smaller streams).

The position and configuration of the Avala Mt. allows intensive water exchange processes within the aquifer of the springs. Avala Mt. system is a segment of the documented hydrodynamic zone characterized by intensive water exchange processes, theoretically reaching a complete exchange of water in 100 years timeframe. The flow and drainage of groundwater in the given conditions is the consequence of gravitational forces. Within the comparable hydrodynamic conditions, atmospheric water infiltrates into local aquifers. Higher content of oxygen and carbon dioxide makes these near-surface water systems aggressive. These gases boost the ongoing weathering of carrier-rocks, in particular, carbonates and silicates (hydrolysis and dissolution of aluminosilicates and carbonate) and also oxidation of sulfides.

The aquifers in the narower area of Avala Mt. can be outlined as a rock assembly characterized by a lower hydrogeological potential (reduced flow ability, water exchange and drainage of groundwater). Also, the entire system of captured springs marks the local fault zones, which indicates that the springs are controlled by the local tectonic discontinuities (faults). Consequently, the faults represent the permeable geological environment.

With exception of the spring "Točak" (accommodated within serpentinite) and „Kraljeva česma" other springs were formed in the Upper Cretaceous sediments- flysch (consists of layers of sandstone and clay, and less often of marl and limestone). The serpentinites, within solid rock body are characterized by the fracture-controlled porosity. Dacites, quartzlatite, lamprophyres, and latites, do not have a significant influence on hydrogeological properties of the rocks. However, these rocks and sulfide ore mineralization can be a source of arsenic and other heavy metals.

Geological events and geochemical evolution of arsenic in Avala`s aquifers

In addition to key geological processes likewise the local magmatic activity, and the circulation of hydrothermal fluids among extensional fault conduits, it seems that another very important geological process have had certainly influenced the sampled subsurface arsenic concentrations. This process is a post-Pliocene – present-day erosion. Present-day relief is a function of different factors formed during the last terrestrial event. However, it is necessary to bear in mind that there have been the two main erosional stages differentiated during the geological evolution of the investigated Avala complex. The initial erosional event was probably induced by a regional uplift that was coeval with the magmatic emplacements accommodated during the process of the Vardar Ocean closure and postdating extension (e.g., Schmid et al., 2008; Spahić & Gaudenyi, 2019). After the new post-collisional transgressive episodes lasting during Miocene ceased, weathering and denudation during the final post-Pliocene erosional stage exposed a large portion of the agglomerated flysch, volcanic and cap-rock Neogene sedimentary material.

After the local Pliocene lakes were drained away, the sedimentary cover was exposed to the surface, atmospheric erosion led by the ancient paleostreams. A detailed analysis of the Quaternary continental genetic forms highlights a dominance of fluvial processes (Marković et al., 1985). After the exposed sedimentary portion was gradually flushed away, the deeper levels of a volcanic complex were further exposed to the atmospheric influence. After denudation and extraction from the complex Avala bedrock system, heavy components tent to percolate towards the nearest recharge area or in the direction of a confined aquifer. The latter is, most likely, comprised of the mixture connecting a fractured magmatic body and surrounding sedimentary rocks. The essential processes, e.g., paleoprecipitation, secondary porosity and overall rock permeability, have directly influenced the spatial mobility of heavy components, likewise arsenic. In addition, the timeframe of the second erosional phase (~3.6 Ma to present day) allowed a sufficient time for additional unroofing and removal of the overburden and the development of secondary porosity. Removal of the overburden thus enabled a dissolution of durable principal arsenic sources – the arsenopyrite-bearing volcanic rocks. Extensional faulting and fracturing underpinned the solubility of arsenic-bearing magmatics, further allowing the development of secondary porosity. The secondary porosity further facilitated a gravitational percolation of dissolved heavy components moving these particles towards a partially compartmentalized principal Avala's aquifers. The essential indicator of the proposed spatial subsurface hydrodynamic compartmentalization is a differential occurrence of the sampled arsenic concentrations from the springs widespread across the investigated complex.

Material and methods

Sample collection

Avala Mountain is abundant with springs characterized by a relatively low water production rate, whereas several springs are additionally not accessible for water sampling or dried out. During the August and September of 2011, groundwater from the springs named: "Velika česma", "Sakinac", "Vranovac", "Točak", "Kraljeva česma", "Ledenac", "Kamenac", "Zuce" and the wells "Avala" and "Zuce" were sampled. Location of the investigated area and the sampling points are presented in the Fig. 1.

The water samples were collected into acid-washed polyethylene bottles and sub-samples for arsenic analysis are immediately acidified with HCl

(1:1) solution (up to pH<2). The samples for detection of heavy metals (Cr, Ni, Pb, Zn, Fe, Mn, Cu) are treated with HNO_3 (1:1) (up to pH<2), pH and electro conductivity (EC) and temperature are additionally analyzed on site.

The water from "Avala" well was re-sampled during March 2012, because suspended compounds occurred during the pumping. This time the water suspension was digested by acid. The applied method here was used in order to consider the correlation between As and the elements Fe, Mn (common for a solid residue appeared in subsurface well waters). Thus, the concentration of the elements measured before and after the treatment records variations/discrepancies.

Analytical methods

The total arsenic concentration is detected by using the AAS-HS technique (AAS-atomic absorption spectrophotometer-Perkin-Elmer 6500, with MHS-15 hydride generation system, Perkin Elmer). The limit of detection of this method is 0.5μg/l. The samples, standard solutions and blank-samples are prepared 24 hours before measuring, by treating the samples with 10% KI solution (10:1) with addition of HCl conc. (10:3).

The main cations: Ca, Na, K, Mg and Si are analyzed by AAS-F (atomic absorption spectrophotometry – flammable technique, Perkin Elmer 6500) after direct aspiration of a no acidified sample into the system. The anions SO_4 and NO_3 are determined by UV/VIS spectrophotometer (Perkin Elmer, Lambda 15), whereby anions Cl and HCO_3 are analyzed by the volumetric titration.

The concentrations of heavy metal Cr, Ni, Pb, Cu, Zn, Fe, Mn are detected by ICP/OES spectrometry (CAP 6500 DUO, Thermo Scientific, UK), after direct aspiration.

Results and discussion

Physicochemical parameters

In order to delineate the origin of arsenic in the sampled waters, including the influence of local geological structure on the subsurface water composition, the main physicochemical parameters are analyzed (Table 1).

Groundwater around Avala structure exhibit rather neutral pH values, low- to medium mineralization with lower temperatures. A predominant anion is HCO_3 with the mean value 392.6 mg/l, whereas predominant cations are Ca and Mg with the mean values of 93.0 and 42.1 mg/l, respectively. Additionally, the mean value of one of the dominant ion - Cl is 59.7 mg/l, and in samples "Sakinac" and "Kamenac" is detected the highest value of As (Table 1).

Piper diagram (Fig. 2) is represented as a projection of cation and anion ternary diagrams into rhombic space.

According to dominant ions the investigated groundwater can be classified into the four types:

- **HCO_3-Ca-Mg** type: water from springs Velika česma, Vranovac, Zuce and well Avala.
- **HCO_3-Cl-Ca-Mg** type: water from springs Sakinac, Kamenac, Kraljeva česma and Ledenac.
- Water of Točak spring belongs to the **HCO_3-Mg-Ca** type.
- Water from Zuce well can be classified as the **HCO_3-Mg** type.

The chemical composition of the studied waters seems to be a function of the geological setting i.e. geological (paleo) environment. Namely, the investigated springs are mainly accommodated in the fault zones that are crosscutting the Cretaceous sediments and serpentinite (Fig. 1) The spring "Velika česma" in the village Beli Potok originates from the contact of limestones, sandstones and marls (flysch sediments) of the Upper-Cretaceous age and sand, sandstone, gravel and marly clay belonging the Mio-Pliocene age. The springs "Vranovac", "Sakinac" and "Ledenac" are formed in limestones and marls of Upper-Cretaceous, which are tectonically damaged due to the magmatic intrusion of the eruptive veins, quartzlatites and latites; the spring "Kraljeva česma" appears from the fault zones in serpentinite, while the spring "Točak" is embedded in fractured serpentinite overlaid by the Neogene conglomerates, gravel, sand and sandy clay (Popović, 2007). The well "Zuce" located in the village of Zuce (35 m deep) is drilled through serpentinites, whereas the spring "Zuce" itself, similarly likewise the spring "Ka-

***Table 1**. Physicochemical parameters of the groundwater samples.*

Parameters	Velika česma	Sakinac	Vranovac	Točak	Kamenac	Kraljeva česma	Ledenac	Zuce spring	Zuce well	Avala well
	1	2	3	4	5	6	7	8	9	10
pH	7.2	7.3	7.5	7.3	7.1	6.9	7.1	7.2	7.3	6.7
T (°C)	12.8	12.1	15.0	16.4	18.1	17.5	11.0	14.1	14.2	16.0
EC (µS/cm)	930	780	460	960	1038	1115	400	560	708	620
TDS (mg/l)	843	650	451	908	740	814	268	544	708	742
dry residue (mg/l)	622.0	522.0	308.0	642.0	570.9	567.2	193.0	369.4	477.8	461.6
hardness (°dH)	29.4	94.4	14.4	30.7	27.3	30.5	7.8	17.7	25.1	21.7
Ca (mg/l)	149	134	72.8	56.4	156	114.4	31.5	91.1	32.4	93.0
Mg (mf/l)	36.5	20.1	17.9	97.9	23.9	62.2	14.4	21.4	88.2	37.3
Na (mg/l)	16.1	9.41	13.5	20.0	12.6	17.2	12.5	15.5	18.9	26.0
K (mg/l)	0.97	1.00	1.77	0.45	2.80	2.40	5.50	2.80	1.90	2.50
HCO_3 (mg/l)	448	305	280	541	337	493	151	350	461	560
Cl (mg/l)	43.0	106	5.60	66.3	165	65.8	31.9	24.8	50.6	7.10
SO_4 (mg/l)	69.3	47.8	31.7	13.0	19.8	22.5	19.9	0.91	2.01	15.2
NO_3 (mg/l)	80.1	25.1	27.4	113	22.6	6.20	1.74	37.9	53.2	0.42
NH_4 (mg/l)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	0.13	<0.01
Fe (ng/l)	0.006	<0.005	0.005	<0.005	<0.005	0.005	0.146	0.010	0.006	<0.005
Cr (mg/l)	<0.003	<0.003	0.003	0.040	0.004	<0.003	0.005	0.006	0.060	<0.003
Mn (mg/l)	0.013	<0.005	<0.005	<0.005	<0.005	0.008	0.120	0.007	0.005	<0.005
Zn (mg/l)	0.007	0.009	0.006	<0.005	0.006	0.007	<0.005	0.008	0.017	<0.005
Ni (mg/l)	<0.005	<0.005	<0.005	<0.005	<0.005	0.009	0.007	<0.005	0.005	<0.005
Si (mg/l)	14.3	13.8	12.8	14.2	26.4	30.2	9.40	20.2	42.8	7.90
As (µg/L)	16.4	34.7	102	<0.5	13.3	43.4	47.7	36.1	6.2	5.0

menac" appears at the Upper-Cretaceous sediments. Water from the exploration well "Avala", located on the western side of Avala Mt. is collected from the fractured flysch sediments at the depth of 90 m (Marković, 2010).

According to the published data and the results of analysis of studied samples it can be concluded that in groundwater collected from the springs accommodated within the Upper Cretaceous sediments the dominant ions are Ca and HCO_3. A higher concentration of Mg and the detected presence of Cr in some water samples (Table 1) can indicate the influence of serpentinite. Ni is detected in "Kraljeva česma" spring and "Zuce" well, similarly marking the influence of serpentinites. The other heavy metals such are Pb and Cu were not detected in any of the samples.

In general, chlorides can occur in association with sea water, evaporite sediments and often are documented in a vicinity of active volcanoes (Mullaney et al., 2009). During the Lower Miocene, the most part of the investigated area was overlaid by lacustrine / sea waters, and afterwards (Middle–Late Miocene) there was a deposition of clastic and carbonate rocks (Toljić, 1995; Rundić et al., 2019). During the very process of sedimentation, sea water can be trapped in consolidated and poorly cemented sediments, followed by the post-depositional circulation of fluids. Circulation can cause their dissolution, removal and transport to the eventually overlaying geological entities. Considering the fact that specific hydrogeological conditions are important for concentration level of the components, in particular principal ions, it is possible that Cl ions could be removed very rapidly with fast groundwater flow and accumulated in stagnant conditions.

Nitrates appear in the springs of the north-east side of Avala Mt. Considering the fact that there is a dense population and that there is an unprotected

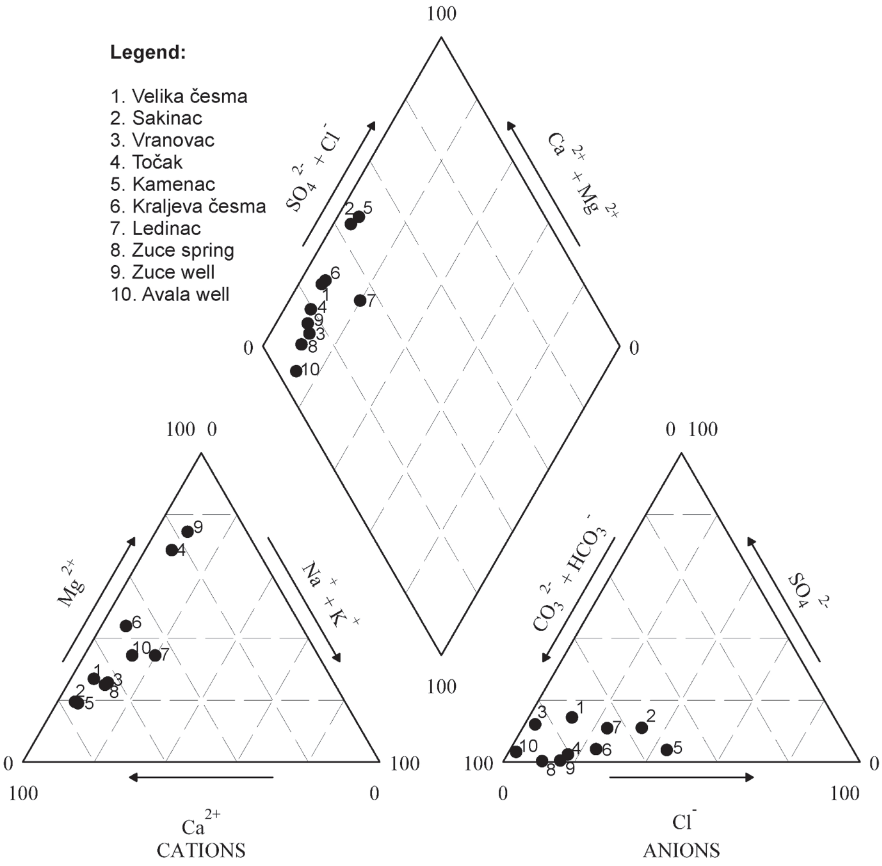

Fig. 2. *Piper diagram of the studied groundwater samples.*

household septic system, the presence of NO_3 ions are likely to be related with local anthropogenic activities.

In the “Ledenac” spring, the concentrations of Fe and Mn have highest levels, along with the presence of NH_4 ions. However, the concentration of the NO_3 has lower values than in the other samples. Such composition can indicate reductive conditions considering the fact that Mn is commonly present in groundwater, in particular in anaerobic or low oxidation conditions (Dalmacija & Agbaba, 2006). Such conditions may also lead to the reduction of Fe (III) to Fe (II). In particular, the exposure to the atmosphere influences (oxidative environment) dissolution of ferrous iron that commonly oxidizes and relatively rapidly precipitates in the form of ferric oxy-hydroxides (Reimann & Birke, 2010). The reduction of Fe and Mn in the lower oxidation states leads to their greater solubility and an increased concentration.

Consequently, reductive dissolution of Fe oxy-hydroxide leads to elevated concentrations of arsenic, because it can depend on releasing of absorbed arsenic forms (Vanderzalm et al., 2010). In addition, redox condition in the environment (groundwater) would reduce As (V) to As (III) in the case of its presence, inducing a possible desorption. The reason can be attributed to a lower affinity of As (III) for adsorption at oxy-hydroxides surface (García-Sánches et al., 2005). Moreover, there are the other differences between the “Ledenac” spring and the rest of water samples: minimum value of Ca, Mg and TDS. The main reason can be the fact that the spring is accommodated within a central part of the Avala volcanic dome, whereas other springs are distributed along its marginal area (Fig. 1). This area could be characterized by more intensive dissolution of bedrocks and intensive drainage and thus accumulation in nearest aquifer.

Relationship between chemical parameters and bedrock

The Pearson’s coefficients (Table 2) introduce possible correlations between the parameters, and suggest similar or different behavior or the origin of elements in groundwater. Evident strong positive relations (significantly correlations 0.6–1.0, p= 0.05) appear between Mg-HCO_3, Na-HCO_3, Mg-Cr, K-Fe, K-Mn, TDS-HCO_3, and Zn-Si.

The highest correlation coefficient (0.996) is observed between Fe and Mn indicating the similar conditions and the mechanism of migration in the sampled groundwater. In addition, the concentration of K could be related to the adsorption-desorp-

***Table 2**. Pearson' s correlation of the parameters.*

	As	Ca	Mg	Na	K	Fe	HCO_3	Cl	SO_4	NO_3	TDS	pH	Cr	Mn	Zn	Si
As	1.00															
Ca	-0.11	1.00														
Mg	-0.53	-0.36	1.00													
Na	-0.51	-0.26	0.55	1.00												
K	0.22	-0.33	-0.47	-0.16	1.00											
Fe	0.22	-0.49	-0.32	-0.25	0.85	1.00										
HCO_3	-0.62	0.11	0.72	0.82	-0.59	-0.67	1.00									
CL	-0.29	0.56	0.07	-0.42	-0.12	-0.21	-0.02	1.00								
SO_4	0.17	0.60	-0.33	-0.37	-0.36	-0.08	-0.12	0.10	1.00							
NO_3	-0.38	-0.07	0.61	0.15	-0.68	-0.34	0.40	-0.01	0.14	1.00						
TDS	-0.66	0.44	0.65	0.47	-0.73	-0.37	0.87	0.38	0.15	0.54	1.00					
pH	0.42	-0.20	0.03	-0.55	-0.36	-0.08	-0.40	-0.04	0.17	0.51	-0.22	1.00				
Cr	-0.45	-0.62	0.81	0.31	-0.26	-0.11	0.33	-0.04	-0.50	0.56	0.25	0.35	1.00			
Mn	0.18	-0.45	-0.31	-0.27	0.81	0.99	-0.63	-0.21	-0.03	-0.31	-0.69	-0.10	-0.12	1.00		
Zn	0.03	0.00	-0.16	-0.27	-0.18	-0.27	-0.06	0.17	-0.54	0.04	0.02	0.39	0.41	-0.25	1.00	
SI	-0.21	-0.09	0.51	0.04	-0.07	-0.27	0.23	0.36	-0.40	0.07	0.27	0.09	0.58	-0.27	0.78	1.00

tion process with Fe-Mn oxy-hydroxide surface. The weak negative correlation between Mg and Ca suggests that these elements generally do not have the same origin, despite these coexist and occur together in carbonates. The strong correlation between Mg-HCO_3 and Na-HCO_3 indicates that erosion of carbonate is not the exclusive source of the documented HCO_3 ions (Mrazovac & Vojinovic-Miloradov, 2011). In general, occurrence of HCO_3, Ca, Mg, K, Na in waters could be the result of hydrolysis of aluminosilicates, in particular of feldspar (orthoclase, plagioclase, albite, anortite; Dimitrijević, 1988; Kouras et al., 2007). The presence of the aforementioned minerals is documented in the Tertiary volcanic rocks of Avala. Therefore, Na, Ca and Mg in the samples partially were derived due to mineral decomposition. On the other hand, the correlation between Cr-Mg, Mg-Si and Mg-Na suggests possible weathering of other minerals such as serpentinites (ultramafic rocks).

The negative correlations coefficient, registered between As-HCO_3 (r= –0.62) and As-TDS (r= –0.66) indicates that HCO_3 and arsenic do not have the same origin, whereas the highest presence is detected in the water samples with lower mineralization (mild weathering driven dissolution of carbonates or alumosilicates). The probable origin could be associated with deeper thermal waters actively flowing along the contact between eruptive veins and Cretaceous sediments. Furthermore, the negative correlation between TDS-As can be related to the water exchange processes. Namely, in the springs accommodated within the aquifer of the hypsometrically elevated area, the lower TDS contents and higher concentrations of arsenic are observed. Moreover, such negative correlation implies that more intensive water exchange processes exist as the higher concentrations of As are. In support of the previous, there is a strong inverse correlation between As and TDS.

The lack of good correlation between Fe-As (Table 2) can be explained by a different behavior of the final products of decay, arsenopyrite and pyrite (Equation 2.). Whereas the iron is deposited in the form of insoluble limonite or amorphous FeOOH, the arsenic which is in the form of arsenate becomes mobile. A high correlation factor between Si-Zn (0.7857) corroborates a hypothesis of adsorption barriers. Elevated concentrations of dissolved Si, followed by decomposition of silicate (in form of H_4SiO_4 at pH=7) result in an increase of the Zn concentration (due to adsorption of cations Zn^{2+} to negative particles of clay, colloidal particles $xSiO_2*yH_2O$ or other negative charged Si-particles).

Sulfates are not well-correlated with the elements, with exception of Ca-SO_4 (0,599). This correlation suggests that SO_4 could have more than one source. Hence, the concentration of SO_4 ions in water is not proportional to the quantity of sulphide which can be regarded as one of the potential sources (in the case of the presence of sulfide ore - deposits rocks) neither with As. The same conclusion is underlined by García-Sánches et al. (2005). Furthermore, the concentrations are influenced by (a) surrounding rocks, (b) the extent of the oxidation zone and a (c) groundwater regime. Groundwater fluctuations and changes of an oxidation-reductive layer cause the concentration fluctuation of the sulphure/sulphates.

Distribution of arsenic and definition of its origin

The range of concentration of inorganic arsenic in Avala´s groundwater is 3.0–102.3 µg/l. The arsenic concentrations are discussed with respect to the domestic and internal regulations: Regulation on Quality and Other Requirements for Natural Mineral Water, Spring Water and Bottled Drinking Water (Službeni list SCG, 2005) as well as regulation of WHO and EU Directive 1998/83/EC Drinking Water. The MAC of arsenic in drinking water defined by the standards is 10 µg/l.

A comparison of the results with the reference value for As, yields that the studied waters (excluding the waters from “Točak” spring and the wells “Avala” and “Zuce”) are enriched by this element.

In order to understand the highest arsenic content from the “Vranovac” spring, the surrounding geology is analyzed more in detail. According to the geological map of Toljić (1995), the vicinity of Vranovac stream/creak can be characterized by hydrothermally altered quartzlatite veins. A similar observation was confirmed on the sampling site during the field trip. A significant presence of hydrothermally altered rocks and the occurrence of arsenopyrite could explain a highest concentration of arsenic in the sampled water of “Vranovac” spring.

The result of chemical weathering of arsenopyrite is explanation of the presence of migrative form and oxidation state As V ($H_2AsO_4/HAsO_4$, at pH=7). This process could be explained by the following mechanism:

$$2FeAsS+7O_2+6H_2O\rightarrow 2FeAsO_4\times H_2O+2H_2SO_4, \qquad (1)$$

by oxidation arsenopyrite is transformed to the scorodite.

This mineral is stable in dry and oxidative conditions. However, in contact with fluids (water) scorodite can be transformed into a mobile arsenic form and insoluble limonite as deposit:

$$FeAsO_4\times H_2O+2H_2O\rightarrow Fe(OH)_3+H_3AsO_{4,} \qquad (2)$$

In the area of Avala Mt., scorodite has not been detected, whereas limonite is documented.

Similarly, arsenic can be transformed to the mobile form from pyrite (in the structure of pyrite, As changes the sulfur atom), which may be initiated by spontaneous oxidation. It occurs especially because pyrite undergoes to oxidation, (due to iron`s affinity to an oxygen):

$$2FeS_2+7O_2+5/2H_2O\rightarrow Fe\ OOH+2SO_4^{2}+2H^{+}, \qquad (3)$$

The final product is limonite or amorphous Fe oxy-hydroxide. Sulfur is oxidized to sulfate, which then has a capability to migrate or remains in the oxidation zone (Dimitrijević et al., 2002).

On the other hand, the lowest concentrations, as well as the concentrations below a detection limit are in the waters formed in the zones of fractured serpentinite (oldest ophiolite-bearing complex of the Avala Mt.). The similar conclusion can be derived from the results of analyses of the water sample collected from the investigated well drilled in 2008 (Zavojnička river, Zuce). The concentration of arsenic was 3.0 mg/l (Tripković, 2008).

The results of detected concentrations of arsenic in the aquatic environment are not the results of the weathering processes only. Their presence and mobility of arsenic forms is a function of chemical environment within the aquifer. Following the arsenic release through the process of pyrite oxidation, a newly formed amorphous Fe OOH plays an important role in controlling the mobility of arsenic in the storage zone. Fe OOH may accommodate a subsequent removal of arsenic, prior its recovery (predominantly attributed to sorption under favorable conditions; Vanderzalm et al., 2011). This conclusion corroborates the experiment presented in the Table 3.

Table 3. *The results of analysis of the water sample from well "Avala"- before and after acid digestion.*

As (μg/l)		Fe (mg/l)		Mn (mg/l)	
As (before the treatment)	As (after the treatment)	Fe (before the treatment)	Fe (after the treatment)	Mn (before the treatment)	Mn (after the treatment)
0.5	6.2	<0.005	15.7	<0.005	0.29

Detection of the concentration of As, Mn, Fe before and after acid digestion of the water suspension sample "Avala" well (water with the solid residue the results) indicates an increase in the total concentrations of arsenic and Fe (sum of the concentrations in water and solid residue). The result suggests that arsenic is deposited along with Fe and Mn. More precisely, it is adsorbed at the surface of ferry oxy-hydroxide particles. Namely, arsenate as a stable form in aerobic conditions can become less mobile. Thus, the As could be removed by the several processes, precipitation or adsorption onto hydrous iron oxides. The fact that hydrous iron oxide has a positive surface charge in most geological environments and preferentially adsorbs anions, whereas manganese oxide is negatively charged and adsorbs cations, provides the suitable explanation of a such distribution (Subramanian at al., 2002). Moreover, the example of this equilibrium could be water of "Ledenac" spring (explained earlier in the text).

In contrast to the "Avala" well, the concentration of arsenic in other springs and other well are elevated because arsenic from ferric oxy-hydroxides particle surface desorbs to the investigated groundwater environment.

Conclusion

The study documents the presence of arsenic, its distribution, and the origin in groundwater of the Avala volcanic complex. This research leads to the following conclusions:

1) Spanning the Late Cretaceous – present-day geological timeframe, the investigated area represents the system with favorable conditions for arsenic subsurface development. Initially, there is a documented presence of hydrothermally altered magmatic rocks including the occurrence of mineralizations, followed by a protracted weathering and atmospheric impact on the particular arsenic-bearing rocks. Secondly, being crosscut by rock discontinuities and deformations, the fractured Avala volcanic complex facilitated a protracted interaction of water percolating throughout these subsurface discontinuities;
2) The occurrence of arsenic in groundwater of the investigated area is of natural origin. Its presence within the detected concentration range could be a result of the two controlling processes: a) expected chemical weathering of minerals such as arsenopirite-pyrite and b) mechanisms such as sorption/desorption commonly associated with the surface or occlusions by amorphous Fe OOH (or limonite);
3) The range of the concentration of inorganic arsenic in Avala´s groundwater is 3.0–102.3 μg/l. The spring with maximum detected concentration of arsenic is "Vranovac", emplaced within the geological domain characterized by hydrothermally altered quartzlatite veins. The lowest concentrations, along with the concentrations below the detection limit are documented within the waters formed in the zone of fractured serpentinite (in the Avala's oldest rock complex). Additionally, the highest concentrations of As were documented in the area of the intense water exchange.

The concentrations of arsenic measured in seven samples exhibit the levels which are above the maximum-allowed values for drinking water (according to the domestic and foreign regulations). A continuous ongoing exploitation of water from these supply sources may impose a risk to human health. Nevertheless, the health risk is rather low considering the fact that the spring waters have just occasionally been used by tourists and local population.

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Резиме

Појава и еволуција арсена у извориштима вулканског комплекса Авала (периферија Београда, Србија)

Арсен је хемијски елемент који, у животној средини, као загађивач може бити присутан из природних и антропогених извора. Иако по заступљености у Земљиној кори заузима двадесето место, због своје токсичности проучавање присуства и садржаја арсена, посебно у пијаћој води све више добија на значају. Томе доприноси податак да дуготрајно уношење арсена у количини од 30–60 μg изазива канцер коже.

Природно порекло арсена у водама везано је за специфичне области-сулфидне минерализације, геотермалне, семиаридне-аридне са високим pH, као и области анаеробних аквифера.

Обзиром да су у испитиваној области вулканско-офиолитског комплекса Авале регистроване појаве сулфидних минерализација, претходна иницијална истраживања указала су на појаву арсена у води појединих каптираних извора, највише посећених од стране туриста. У њима су регистроване појаве садржаја арсена изнад максималне дозвољене (10 μg/l). Стога, ово истраживање представља: 1.) потврђивање датих вредности садржаја As у испитиваним водама; 2.) утврђивање појаве и концентрације у води других доступних извора или бунара; 3.) порекла арсена у подземној води аквифера вулканског комплекса Авале. Такође, у овом раду дефинисан је катјонско-анјонски састав вода и корелација између главних компонената/микрокомпонената. Сходно томе, доведен је у везу састав подземне воде и литостратиграфских јединица које су присутне на површини.

Испитивани узорци подземних вода спадају у групу мало до средње минерализованих,, при чему су најдоминантнији катјони Ca и Mg и анјони HCO_3 и Cl.. Хемијски састав одражава геолошке карактеристике испитиване области, јер су извори смештени у оквиру испуцалих зона тј. локално развијених пукотина које пресецају Авалски офиолитски комплекс (серпентинити). Присуство Ni, Cr и Mg, као и значајна корелација између Cr и Mg указује на вероватан утицај серпентинита на састав воде. С друге стране, одсуство значајне позитивне корелације As са наведеним компонентама, може сугерисати на другачије порекло овог елемента. Оно је највероватније везано за дубље циркулисање термалних вода на контакту магматских интрузија које пробијају сам офиолитски комплекс укључујући и околни седиментни пакет кредне старости.

Резултати хемијских анализа су показали да опсег концентрација As у испитиваним узорцима износи од 3.0–102.3 μg/l. Најниже концентрације или одсуство As карактеристично је за воде формиране у испуцалим серпентинитима које припадају најстаријем офиолитском комплексу источне Вардарске зоне. Максимална концентрација регистрована је у извору смештеном у области хидротермално измењених стена уз присуство арсенопирита, односно пирита. Додатно, резултати хемијске анализе суспендованог узорка воде бунара „Авала”, пре и после киселинске дигестије на садржај елемената As, Fe и Mn указали су на могућ процес адсорпције-копреципитације As услед таложења Fe- и Mn- оксихидроксида.

Сумирано, појава арсена у подземним водама Авале је природног порекла јер су постојали геолошки предуслови за његово присуство. Они су везани за хидротермалне измене магматских стена и појаве сулфидне минерализације праћене хемијском алтерацијом минерала. Додатно, томе доприносе екстензионе деформације као и испуцалост стена магматског комплекса Авале која омогућава циркулацију подземних вода. Опсег концентрација детектованих у изворима и бунарима последица је равнотеже између процеса хемијске алтерације минерала типа арсенопирита и пирита, као и процеса адсорпције десорпције-копреципитације арсена са Fe- оксихидроксидима (у кристалном - лимонит или аморфном облику).

Свакодневном дуготрајном употребом подземне воде са извора у којој је доказано присуство As у концентрацијама изнад 10 μg/l може представљати висок ризик по људско здравље.

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