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THE ORIGIN OF ARSENIC IN SOILS AND GROUNDWATER OF THE PANNONIAN PART OF CROATIA

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Arsenic content in surface layer (0-25 cm) varies from 0.9 mg/kg soil to almost implausible 490 mg/kg. The reason for the highest content in hydromorphic soils should probably be sought in recent history. It is less probable that the reason for the increased arsenic content in hydromorphic soils is the geological origin of rocks in river valleys. It is more probable that the reason for the increased arsenic content is river flooding and changes in river flows in the recent past. Based on 208 groundwater samples from 12 locations of Koprivnica-križevci county during 2009-2012, the range of arsenic concentration from <0.1 µg/l to 25.4 µg/l was determined. The concentrations are, generally, very low (<0.1-6.9 µg/l) on the most of locations. The values in Vratno and Kolarec locations indicate an increase in arsenic concentration above the permitted values. Groundwater that is rich with arsenic is result of the natural mineral weathering of rocks.

Key words: origin of arsenic, soil, groundwater.

Podrijetlo arsena u tlu i podzemnim vodama panonskog dijela Hrvatske. Sadržaj arsena u površinskom sloju tla (0-25 cm) varira od 0,9 mg/kg do skoro nevjerojatnih 490 mg/kg tla. Razlog za najviši sadržaj u hidromorfnim tlima vjerojatno treba tražiti u novijoj povijesti. Manje je vjerojatno kako je razlog povećanog sadržaja arsena u hidromorfnim tlima geološko podrijetlo stijena u riječnim dolinama. Vjerojatniji razlog povećanog sadržaja arsena su poplave rijeke i promjene u riječnim tokovima u nedavnoj prošlosti. Na temelju 208 uzoraka podzemnih voda, iz 12 lokacija Koprivničko-križevačke županije u razdoblju od 2009. do 2012. godine, određen je raspon koncentracije arsena od <0,1 µg/l do 25,4 µg/l. Koncentracije su općenito vrlo niske (<0,1-6,9 µg/l) na većini lokacija. Vrijednosti na lokacijama Vratno i Kolarec pokazuju porast koncentracije arsena iznad dopuštenih vrijednosti. Podzemne vode bogate arsenom rezultat su prirodnog mineralnog trošenja stijena.

Ključne riječi: podrijetlo arsena, tlo, podzemne vode.

INTRODUCTION

Arsenic is a chalcophile trace element, 53rd most abundant element in the Earth's crust. Arsenic is found in the following oxidation states: As³⁻, As⁰, As³⁺, As⁵⁺, while As⁰ and As³⁺ are found under reducing conditions. The ionic forms AsO₂⁻, AsO₄³⁻, HAsO₄²⁻, H₂AsO₃²⁻ are predominant in soil and they are also the most mobile, but arsenic can also be found as As³⁺ and As⁵⁺.

Arsenic in soil binds to Al and Fe hydroxides, clay fractions and organic matter, as well as calcium and phosphorus compounds [1]. Kabata-Pendias [2] states that a smaller part of arsenic is mobile in soil while the most part of it is strongly bound to sesquioxide and is unavailable to plants. Because of its toxicity and distribution in the environment, arsenic affects human health

and nowadays it is one of the recurring themes of global thinking and action aimed at protecting the environment. Arsenic occurs as a component of more than 200 minerals in the values ranging from a few promilles to a few percent. In 60% of cases it appears in the form of arsenate, 20% in the form of sulphide ores and sulfosalts, and the rest is in the form of arsenic, arsenite, oxides, silicates and elemental arsenic. Smedley and Kinniburgh [3] state that the content of arsenic in igneous rocks is 1 to 15 mg/kg, while volcanic rocks have a somewhat higher content of arsenic. In sedimentary rocks the content of arsenic ranges from 5 to 10 mg/kg. Metamorphic rocks that are formed by weathering of igneous and sedimentary rocks contain arsenic at a concentration of 5 mg/kg. Kabata-Pendias and Pendias [4], as well as Geochemical atlas [5], state that the content of arsenic in natural soil ranges from 0.1 to 40 mg/kg soil. Bissen and Frimmel [6] report that natural sources of arsenic contamination include volcanic activity, dissolution of minerals that contain arsenic and, in recent years more frequent, forest fires. Based on the previous studies, it has been estimated that the volcanic eruptions emitted 17,150 tons of arsenic into the atmosphere, and 27 tons into the oceans [7].

Arsenic and its compounds are mobile in the environment. Weathering of rocks converts arsenic sulfides, or other compounds, to arsenic trioxide which enters by dissolution into rain or groundwater [8]. In addition to the normal levels of arsenic in soil or water, people could be exposed to higher levels in several ways, as is the case in areas containing unusually high natural levels of arsenic in rocks which can lead to unusually high levels of arsenic in soil or water. People living in an area like this could take in elevated amounts of arsenic in drinking water [9]. The potential toxicity and availability of arsenic in the soil, water and in the environment is dependent on several

factors including pH, redox potential and presence of ligands. The rate of arsenate adsorption decreases as pH and silicic acid concentration increased. Large concentrations of phosphate, bicarbonate, silicate or organic matter can enhance desorption of arsenic [10, 11].

Hence, it is very important to evaluate arsenic concentration and influence of naturally present ligands on the absorption of arsenic on surfaces with variable charge and to determine the level of contamination [10, 12, 11]. Well-known groundwater areas that have high concentrations of arsenic have been found in different countries around the world [11]. Natural problem areas of groundwater with arsenic tend to be found in two types of environment: in inland or in strongly reducing aquifers often derived from alluvium [11]. Contamination of groundwater with naturally present inorganic arsenic was determined in some areas [13]. Prolonged drinking of such water risks the development of diseases; therefore, the important preventive is to assess the concentration of arsenic in water [14].

Contamination of groundwater with arsenic has been evidenced in the Pannonian part of Croatia. Hydro-chemical results suggest that the occurrence of arsenic in the groundwater depends on the local geological, hydrogeological and geochemical characteristics of the aquifer [15]. A health risk assessment model was applied to calculate cumulative exposure to arsenic, because toxic and carcinogenic risks are a result of drinking groundwater contaminated with arsenic in the Pannonian part of Croatia [16].

The basic aim of this paper is to try to determine the reasons for the increase in arsenic content at certain locations in the Pannonian part of Croatia. Using the data collected so far, a more detailed and systematic investigation of soil and groundwater contamination by arsenic will be conducted. The aim of this research is:

1. To determine the types of soil in the study area and different land use of soils;
 2. To determine the content of arsenic in particular soil types and land use;
 3. To expose the assumption about the origin of arsenic in particular soil types, based on collected and systematized data;
 4. To determine the total arsenic concentration in groundwater sources at locations of north-western Croatia, in Koprivnica-križevci county (part of Pannonia);
- To estimate the origin of arsenic in groundwater.

MATERIALS AND METHODS

This study integrates the results of determining chemical parameters of 1088 soil samples and the content of arsenic in 961 samples. Soil samples were collected at various locations in the Pannonian region of Croatia (Figure 1. A) in the period from 1989 to 2015. Composite soil sampling was carried out according to land use: forestry land, agricultural land and industrial land use – technosols. Regarding the agricultural and forestry soils, the following are represented in the research: Arenosols, Cambisols and Luvisols (automorphic), and Fluvisols, Luvisols, Gleysols and Stagnosols (hydromorphic) [17, 18]. The industrial usage (Technosols) represents a borehole working area of oil or gas wells. It is a soil which has been used for decades as the area from which hydrocarbons are extracted. When the oil/gas field has been discovered decades ago, their original intention use was abandoned - agriculture or forestry. In order

to ensure unobstructed extraction of hydrocarbons, a borehole working area was made (land-use conversion was carried out) within which mining works were implemented. Outside of this area, soils have continued to be used in agriculture or forestry. These enclosures, in accordance with the number of wells from which hydrocarbons were extracted, ranged from 750 m² to 1500 m².

When the extraction of hydrocarbons was completed, there was no need for borehole working areas. Upon completion of the rehabilitation, the borehole working area is restored to its original purpose (agriculture or forestry) or it is converted into construction land.

Soil samples were taken from the remediate drilling area and the surrounding soil, which borders the borehole region. Methods used to determine the studied parameters are given in Table 1.

Table 1. Methods used in investigations

Tablica 1. Metode korištene u istraživanju

Analysis	Method
Preparation of soil samples for chemical analyses	ISO 11464:2004
Soil quality – Determination of soil organic matter	Modified ISO 14235:1998
Determination of pH in KCl, (1:2.5, w/v)	Modified ISO 10390:2005
Extraction of trace elements soluble in aqua regia	ISO 11466:2004
Soil quality - Determination of trace elements (ICP-AES)	ISO 22036:2008

In this paper Koprivnica-križevci county was targeted to assess the groundwater quality, including arsenic contents. This area is located between 46°10'N and 16°50'E and covers an area of 1748 km². It is part of Pannonia (Figure 1. B).

The first part of study area (Podravina) belongs to the catchment area of the river Drava (locations Ivanščak, Delovi, Đurđevac, Miholjanec, Šemovci, Hampovica, Budančevica). At the southeastern part, gravel-sand aquifer is prevailing. Cover of the aquifer consists of dust, sand and clay with a significant proportion of quicksand and swampy loess. There is no unique hydrogeological regime existing in the aquatic region. The effect of the river Drava on the direction of the groundwater flow is obvious in the zone width of 2 to 3 km along the river Drava. In this zone, groundwater imitates the regime of river Drava during the year. The supply of the aquifer layer is done through infiltration of precipitations through the low permeable cover, as well as through leaching of the Drava river bed in the upstream area. The quality of natural water changes from location to location [19].

Mountain Kalnik dominates on the northwestern hydro-geological area of Koprivnica-križevci county (locations Vratno and Kolarec) [20]. The most prominent parts were built from the Paleogene and Neogene rocks while the northern area is built of the Mesozoic deposits. Massif of Kalnik is built of porous

lime dolomite breccia and permeable to semi-permeable Tortonian deposits. In the surface area, deposits represent collector of rainfall in the deeper layers of the reservoir of groundwater that is 400 m deep. It is lime dolomite aquifer.

Some parts on northwest hydro-geological area stretch on the Pleistocene terrace (Trstenik, Vojakovački Osijek and Dedina). Beneath 7 to 9 m of covering clay there is a 9 m thick aquifer layer that consists of gravel and sand of different granulation. Beneath this layer there is a thin layer of coal, clay and loess clay. The cover is made of clay [21].

During 2009-2012 a total 208 samples of groundwater were taken (4 times per year). The groundwater quality has been assessed systematically for all samples and from all 12 locations that are sources of public or local water supply (Figure 2). Samples were collected according to HRN ISO 56667-5:2000 [22] in clean polyethylene bottles (1 l volume) for laboratory analysis.

The water sampling from sources was done after the release of water, in duration of 2 to 3 minutes, on the outlet of a water supply system. Samples for transportation were stored in the portable fridge, in the dark and at 1 to 5 °C. After delivery to the laboratory, samples were stored at the same temperature until the analysis (within 24 hours). The method (atomic absorption spectrophotometry-AAS) to determine arsenic in water samples was HRN EN ISO 15586:2008 [23].

THEORY AND/OR CALCULATION

Halamić et al. [24] found that the arsenic content in Croatian soils varies from 1.8 to 60 mg/kg soil with an average value of about 14 mg/kg soil. Halamić and Peh [25] state that in Posavina and Podravina the arsenic content ranges from 0.5 to 92 mg/kg

soil, with a median of 10 mg/kg soil. The same authors state that the highest content was determined for Molve and Kalinovac area. Lozo [26] has concluded, based on 1000 processed samples, that the average arsenic content in the Pannonian part was

approximately 14.4 mg/kg soil, while the maximum content was 490 mg/kg soil.

Kisić [27] states that metallurgical industry and glass manufacturing are major anthropogenic sources of arsenic and its compounds. During the processing of copper, lead, cobalt ores and ores of silver, arsenic compounds such as arsenic oxide (As_2O_3) are released. The same author states

that a significant source of anthropogenic pollution of soil by arsenic is the combustion of urban solid wastes and the use of chromated copper arsenate compounds in the production of wood preservatives. Incorrect application of arsenic based protective agricultural products can cause an increase of arsenic content in soil.

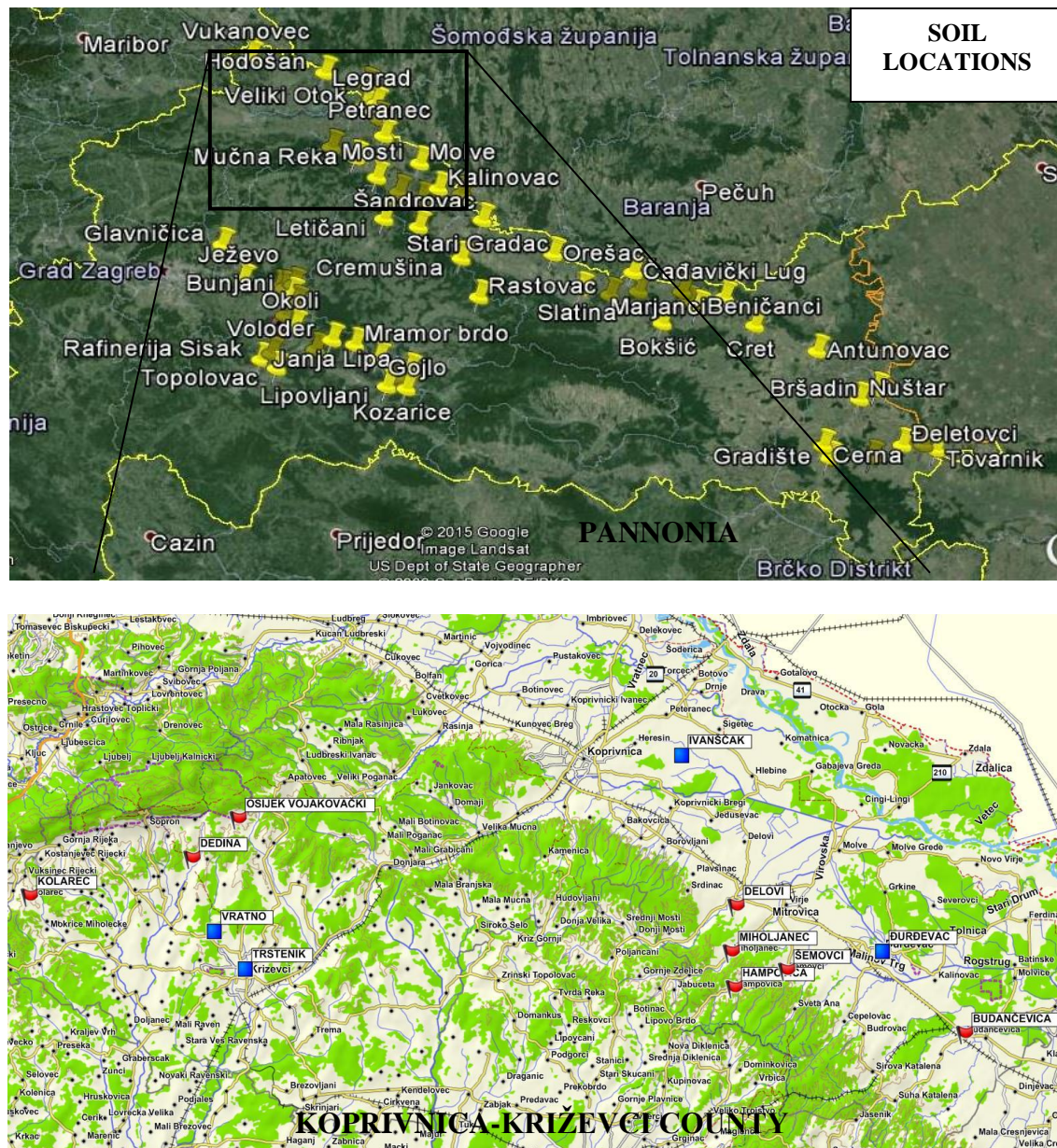


Figure 1. A) Soil and B) water sampling locations
Slika 1. Lokacije uzorkovanja A) tla i B) vode

RESULTS AND DISCUSSION

Tables 2 and 3 show soil reaction and organic matter content in the investigated soils. Table 2 shows that automorphic and technosols are dominantly characterized with neutral reaction, however acidic and slightly acidic reaction was determined in other soils. Since automorphic soils developed on loess materials that have neutral reaction, it was expected that neutral reaction will be determined in these soils. The reason for a neutral reaction in technosols is the application of lime materials for the

rehabilitation of soils in the process of closing drilling pits [27]. Parent substrate on which hydromorphic soils are formed is the reason for their more or less acidic reaction. In terms of organic matter, all soils are characterized by poor humus content, except for the forest soils which are characterized by rather high humus content. The lack of organic matter in soils (excluding forest soils) in the Pannonian part of Croatia was confirmed in this study also.

Table 2. Soil pH of investigated soils

Tablica 2. Reakcija istraživanih tla

	Automorphic	Hydromorphic	Agriculture	Forestry	Technosols	Mean
Mean	6.50	5.97	5.56	4.84	6.70	6.09
Median	7.04	6.12	5.39	4.52	7.05	6.34
Minimum	3.51	3.29	3.42	3.29	3.37	3.29
Maximum	12.71	12.06	7.86	7.56	12.71	12.71
Mark	Neutral	Moderately acid	Slightly acid	Slightly acid	Neutral	Moderately acid
Number of soil samples	284	804	340	137	611	1088

Table 3. Content of soil organic matter, %

Tablica 3. Sadržaj organske tvari tla, %

	Automorphic	Hydromorphic	Agriculture	Forestry	Technosols	Mean
Mean	2.9	3.0	3.1	4.8	2.5	3.0
Median	2.4	2.5	2.6	4.8	1.8	2.5
Minimum	0.8	0.2	0.8	0.6	0.4	0.2
Maximum	11.7	33.6	14.1	11.7	33.6	33.6
Mark	Poorly humified	Poorly humified	Poorly humified	Highly humified	Poorly humified	Poorly humified
Number of soil samples	284	804	340	137	611	1088

Table 4 shows the arsenic content in the surface layer (0-25 cm - horizontal distribution), while Table 5 shows the arsenic content to the depth of 100 cm (vertical distribution). The values displayed, especially the maximum that's established, indicate a marked increase in arsenic content in relation to the average content in this part of Croatia [25]. As shown in Table 5, some locations recorded an increase of arsenic content in deeper layers (25-50 and 50-75 cm). Since the values listed above were determined in subarable layers it is very difficult to compare them with the current human activity. The highest values established for arsenic, regardless of the method of land use, were registered in the wider area of Molve and Kalinovec in Podravina [28, 25].

In order to determine the origin of arsenic, we used the argumentative method. At the very beginning, the extraction of hydrocarbons was excluded as a reason for increased arsenic content, since the increased content of arsenic was not determined in the area (technosols) which was affected by mining operations. Since the highest arsenic content was registered in agricultural soils, and considering that plenty of pesticides are arsenic based, agricultural activities (increased use of protection products) were the next theoretical reason for increased arsenic content. This theory was ruled out since the highest values were determined in the agricultural areas where hardly any protection products were applied, such as meadows and pastures [29]. The confirmation for the theory that protection products are not the reason for increased arsenic content is also found in the established levels of arsenic in forest soils. Increased content of arsenic was also partly determined in deeper horizons of these soils (Table 5). It is well known that conventional pesticides are almost never used in the forest area.

The above specified points out that the reason for increased arsenic content should be sought for in relief characteristics and time of formation for the investigated soils. Automorphic soils are the only soils in which an increased arsenic content was not determined in the horizontal nor the vertical distribution. The probable reason is their position in the relief and time of their formation. These soils were formed in the Pleistocene on the older Würm terrace of the Drava River, which is made of loess and loess-like deposits [30]. They were formed beyond the reach of flood, as well as groundwater of the Drava River and other watercourses. Compared to the current riverbed of the Drava River this terrace is elevated by 10 to 30 meters. Soils that are formed on this terrace have never been affected by the flood waters of the Drava River. Soils, in which increased arsenic content was established, were formed in the Holocene on the younger river terrace which covers a narrow area along the riverbed of the Drava River. These soils have been formed on alluvial deposits that have formed in the last 10-15 thousand years in which the Drava River changed its course. This whole area is directly exposed to high groundwater but also to flood waters of the Drava River. Before embankments were built during a period of high water levels, the Drava River used to flood so much that it would reach the higher Pleistocene terrace.

Since that time the following invocation is very often included in prayers in Podravina villages: 'Deliver us, Lord, from the lightning and storms which cause the Drava River to flood, and save us'. With the construction of embankments, flooding of the surrounding areas has been prevented, but the damage done by the Drava River during the floods of 1810, 1812, and especially 1827, remained forever [31]. We believe that during these floods the materials that contained increased arsenic content were deposited from the higher areas of the

Drava River (Austria, Hungary, and Slovenia). Penetration of the Drava River into a wider area was prevented after the construction of embankments. In some cases the Drava River would penetrate the embankments, for example, in 1850, and threaten the areas of Peteranec, Pitomača, Đurđevac, Virje and Novigrad. During these floods, the content of arsenic in the investigated soils had probably also increased. Skála et al. [32] and Toth et al. [33] had similar observations about the origin of arsenic in the soils of this part of Europe.

The next evidence for this theory on the origin of the arsenic is found in elevations of the investigated area. The area between the villages of Molve, Novo Virje and Ferdinandovac, considering the

elevation, is the lowest. In general, the right bank of the Drava River in this area is lower than the left bank, so in the event of flooding the water would overflow the right bank before the left one. Compared to the highest peak of the village of Molve, which is located 2-3 km from the Drava River, meadows that are found between Molve and the Drava River are at a lower elevation for 10 to 15 meters. Before the construction of embankments this was the region where the Drava River would mostly flood and retain after the flood for the longest period.

The stated hypothesis on increased arsenic content should be tested by more accurate horizontal and, especially, vertical studies on arsenic content in the investigated soils.

Table 4. Content of arsenic in surface layer (0-25 cm), mg/kg soil

Tablica 4. Sadržaj arsena u površinskom sloju (0-25 cm), mg/kg tla

	Automorphic	Hydromorphic	Agriculture	Forestry	Technosols	Mean
Mean	10.7	14.8	14.6	13.9	14.4	14.4
Median	9.5	10.0	10.0	8.9	11.0	10.0
Minimum	3.4	0.9	1.1	2.0	0.9	0.9
Maximum	31.0	490	490	267	143	490
Number of soil samples	226	735	297	132	532	961

Table 5. Content of arsenic in surface and subsurface layers (0-100 cm), mg/kg soil

Tablica 5. Sadržaj arsena u površinskim i podzemnim slojevima (0-100 cm), mg/kg tla

Depth	Automorphic	Hydromorphic	Agriculture	Forestry	Technosols	Mean
	minimum - maximum					
0-25 cm	5.6 - 7.2	8.2 - 348	5.6 - 348	8.2 - 68	8.8-16.4	32.2
25-50 cm	4.5 - 5.9	14.8 - 446	4.5 - 446	14.8 - 204	9.9 - 21.8	45.2
50-75 cm	2.7 - 4.1	12.9 - 268	2.7 - 147	12.9 - 268	12.4 - 184	38.8
75-100 cm	2.7 - 10.0	24.4 - 62	2.7 - 74	24.4 - 62	8.8 - 92	10.3
Number of soil samples	8	23	16	8	7	31

The range of arsenic concentration in groundwater of the study area was determined from $<0.1 \mu\text{g/l}$ to $25.4 \mu\text{g/l}$. At a regional scale, arsenic concentrations in groundwater of Koprivnica -križevci county generally are very low ($<0.1 - 6.9 \mu\text{g/l}$) on the most of locations. However, the values displayed in Figure 2 indicate a marked increase in arsenic concentration on two locations, Vratno (maximum $25.4 \mu\text{g/l}$) and Kolarec (maximum $18.8 \mu\text{g/l}$).

The results obtained suggest that biogeochemical processes controlling arsenic concentration in the groundwater are location-specific [8, 10]. Distribution of arsenic could be linked to different location related parameters such as mineralogy and local hydrology. The rate of arsenic

adsorption is decreased in the presence of silicate, bicarbonate or possibly organic matter and it enhances desorption of arsenic. Development of strongly reducing conditions at near neutral pH can lead to desorption of arsenic from mineral oxides and also to the release of arsenic [9, 11]. Therefore, it is assumed that rocks that are rich with silicates and carbonates, as well as the reducing conditions of aquifer (at a depth of 400 m), can increase concentration of arsenic at Vratno and Kolarec locations [34]. Estimation of spatial variations in groundwater was conducted in the Pannonian part of Croatia and the main geochemical processes responsible for high arsenic concentration in the groundwater were analysed.

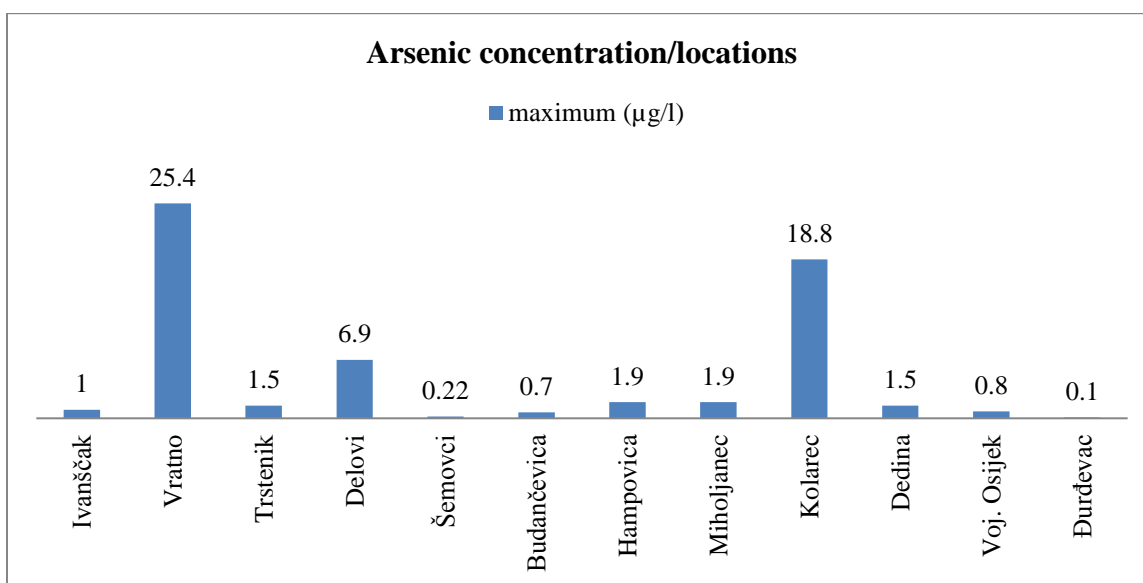


Figure 2. Maximum arsenic concentration in groundwater on specific locations.

Slika 2. Maksimalna koncentracija arsena u podzemnim vodama na određenim lokacijama.

It was evidenced that higher arsenic concentration in groundwater depends on the evolution, local geology, hydrogeology and different geochemical characteristics of the aquifer [16]. In the eastern Croatia arsenic is associated with sulphides and iron in the most of arsenic contaminated samples [15]. Based on classification of samples according to the concentration of arsenic (arsenic-safe:

$< 10 \mu\text{g/l}$ and arsenic contaminated: $>10 \mu\text{g/l}$) one can see that groundwater in most locations is safe. Concentrations are below maximum arsenic level ($10 \mu\text{g/l}$) of current Croatian Regulation [34]. In some researches it was shown that 63% of the groundwater contained arsenic in the excess of $10 \mu\text{g/l}$, 19.6% had arsenic concentration between 100 and $300 \mu\text{g/l}$ and 5% of the water

samples contained arsenic above 300 $\mu\text{g/l}$. The excess of arsenic concentration in drinking water over prolonged periods is likely to cause primary, secondary and tertiary health effects and is a serious cause of concern [35, 36]. In north-western part of Croatia (study area) it was revealed that 25% of the drinking water samples from Vratno contain arsenic excess of 10 $\mu\text{g/l}$. At this location the average arsenic concentration is 10.7 $\mu\text{g/l}$. The average arsenic concentration at Kolarec location was 6.3 $\mu\text{g/l}$ and most samples are arsenic-safe, however, concentrations occasionally exceed the maximum allowable value. According to some researchers, arsenic in water is linked with increased cancer risk or other health effects that come from populations in relatively high exposure areas ($>100 \mu\text{g/l}$) [35, 36]. In the majority of the groundwater samples collected from other locations on study area the results confirmed that arsenic level was significantly lower than 10 $\mu\text{g/l}$ (maximum permissible concentration of Croatia regulation, USEPA, WHO, EU Journal). Low concentrations of arsenic in water are also indicated in some other areas [14]. In the most locations of study area, arsenic pollution of both natural and anthropogenic origin has not been indicated. The results of soil analysis indicates that in

some parts of the Podravina (area along the river Drava) arsenic contents is elevated as a result of the evolution of the soil around the river Drava. That phenomenon has not contributed to the increased concentrations of arsenic in the groundwater in this area above permitted values for now. However, Figure 3 shows the highest maximum concentration of arsenic recorded at the Delovi location which extends in the area where arsenic contents in soil is determined in higher values. It is assumed that there is a link between increased arsenic in the soil and maximal arsenic value in groundwater in this area. A characteristic feature of groundwater areas with high arsenic concentration is a large degree of spatial variability in arsenic concentrations, and it may be difficult to reliably predict the likely concentration in some location. Figure 3 shows variability of arsenic concentration at Vratno location during 2009 to 2012 and Kolarec locations indicate an increase in arsenic concentration above the permitted values. Groundwaters that are rich with arsenic are result of the combined effects of reducing conditions of aquifer, mineral weathering and high evaporation rates which may have an impact on the variability of arsenic [8, 9, 11].

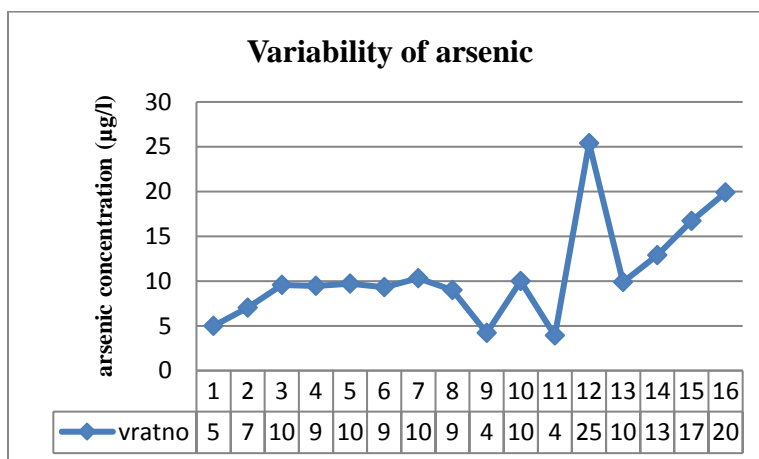


Figure 3. Variability of arsenic in groundwater at Vratno location (2009-2012).

Slika 3. Varijabilnost arsena u podzemnim vodama na lokaciji Vratno (2009.-2012.).

Based on the results one can conclude that arsenic-affected aquifers are restricted to certain area. In general, these results of soil and groundwater analysis demonstrate the importance of evaluating arsenic concentrations and the influence of its natural presence on the variability of arsenic. According to results conducted in the Pannonian part of Croatia the content of

total arsenic varies. On some locations it is not clear whether the cause is only of natural origin or have repercussions of anthropogenic actions from many years ago influenced. In order to determine the exact origin of arsenic in this area, different soil and groundwater analysis should be taken into account and compared with the other physical and chemical parameters.

CONCLUSION

According to the research conducted in the Pannonian region of Croatia the content of total arsenic varies from 0.9 mg/kg soil up to 490 mg/kg soil. The average value of arsenic is 14.4 mg/kg soil. The highest value of arsenic is 490 mg/kg soil, found in the surface layer of agricultural soil. We believe that the reason for the increased arsenic content is flooding and the change of the Drava River flow in the recent past during the Holocene.

It is widely known that in the first half of the last century, the impure waters from factory areas were discharged during the periods of high water levels. At that time there were no defensive embankments and during the floods the water would spread across flooded areas.

In order to determine the origin of arsenic in this area more detailed vertical and horizontal soil sampling should be performed. Different chemical forms of representation of arsenic should be taken into account and compared with the parameters of physical, chemical and microbiological processes in the soil. This study demonstrates the results of determination of arsenic concentration in groundwater that was collected in Koprivnica-križevci county, which is a part of Pannonia. The results point that concentration of arsenic was in the range of <0.1 µg/l to 25.4 µg/l. High concentration of

arsenic (up to 25.4 µg/l) was determined in one location only (Vratno). In location Kolarec, arsenic concentration was determined periodically above maximum allowed values. It was concluded that higher arsenic concentrations were related to naturally present concentrations. Samples collected from other locations in study area have confirmed that arsenic level was significantly lower than maximum allowed values. In these locations arsenic pollution both of natural and anthropogenic origin has not been indicated, however, relation between higher arsenic content in soil and the maximum arsenic concentration in groundwater of Delovi source in Podravina (area along the river Drava) was determined.

Information relating arsenic concentration in different locations of study area will help to broaden the knowledge in this field, especially results which indicate high arsenic concentration caused by the local geochemical structure which includes deposits of arsenic. Such research should be continued in more detail in order to eliminate the dilemma about the origin of arsenic in some locations. The results of the present study should be compared and consolidated with the results of investigations in Pannonian part of Croatia. That way, researches will contribute to a lower influence of arsenic on human health in this area.

REFERENCES

- [1] D.C. Adriano, Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals, 2nd ed. p. 861. Springer-Verlag. New York, 2001.
- [2] A. Kabata-Pendias, Trace elements in soils and plants, 4th ed., Taylor & Francis Group, CRC Press Boca Raton, p. 534, 2011.
- [3] P.L., Smedley, D.G. Kinniburgh, A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry* 17 (2002) 517-568.
- [4] A. Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants 2nd ed., CRC Press, Boca Raton, 1992.
- [5] Geochemical Atlas of Europe. R. Salminen Part I. Interpretation of Geochemical Maps, 117 p. Otamedia Oy, Espoo, 2005.
- [6] M. Bissen, F.H. Frimmel, Arsenic - a review Part I: Occurrence, Toxicity, Speciation, Mobility. *Acta hydrochimica et Hydrobiologica*. 31, (2003), 9-18.
- [7] WHO, Guidelines for Drinking-Water Quality: Addendum to Volume 2, Health Criteria and Other Supporting Information, 2nd ed., World Health Organization, Geneva, 1998.
- [8] M.K. Badal, K.T. Suzuki, Arsenic round the world: a review, *Talanta*, 58, 2002, 201-235.
- [9] C.H. Selene, J. Chou, C.T. De Rosa, Case studies – Arsenic, *International Journal of Hygiene and Environmental Health*, 206, 2003, 381-386.
- [10] C.A. Waltham, M.J. Eick, Kinetics of arsenic adsorption on Goethite in the presence of sorbed silic acid, *Soil science society of America Journal*, 3, 2002, 818-825.
- [11] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Applied Geochemistry*, 17, 2002, 517-567
- [12] A. Sallau, A. Momoh, M. Opuwari, U.A. Lar, S.A. Akinyemi, An overview of trace elements in soils of Keana-Awe Brine-Fields, Middle Benue, Nigeria. *Transactions of the Royal Society of South Africa* DOI:10.1080/0035919X.2016.1229698, 2016.
- [13] M.N. Asadullah, N. Chaudhury, Poisoning the mind: arsenic contamination of drinking water wells and childrens educational achievement in rural Bangladesh, *Economics and Education Review* 30, 2011, 873-888.
- [14] I. Komorowicz, D. Baralkiewicz, Determination of total arsenic and arsenic species in drinking water, surface water, wastewater and snow from Wielkopolska, Kujawy-Pomerania and Lower Silesia provinces, Poland, Environmental monitoring and assessment, DOI: 10.1007/s10661-016-5477-y, 2016.
- [15] M.U. Bošnjak, S. Fazinić, Ž. Duić, Characterization of arsenic-contaminated aquifer sediments from eastern Croatia by ion microbeam, PIXE and ICP-OES techniques, *Nuclear Instruments and methods in Physics, Research Section B: Beam interactions with materials and atoms*, 312, 2013, 23-29.
- [16] M.U. Bošnjak, K. Capak, A. Jazbec, C. Casiot, L. Sipos, V. Poljak, Ž. Dadić, Hydrochemical characterization of arsenic

contaminated alluvial aquifers in Eastern Croatia using multivariate statistical techniques and arsenic risk assessment, *Science of the Total Environment*, 420, 2012, 100-110.

[17] IUSS Working Group WRB, World reference base for soil resources 2006. 2nd edition. World Soil Resources Reports No. 103. FAO, Rome, 2006.

[18] S. Husnjak, *Sistematika tala Hrvatske. Udžbenici Sveučilišta u Zagrebu*, 373, 2014.

[19] D. Mayer, K. Urumović, B. Hlavnjak, H. Gold. Hydrogeological study of the development of water source Ivanščak. Faculty of mining, geology and petroleum Engineering, Zagreb, 1996.

[20] A. Šimunić, *Hydrogeology of Kalnik*, Croatian Geological Survey, Zagreb, 1984.

[21] D.M. Sebastijan, V. Britvić, Feasibility study for obtaining a water management permission of Trstenik source, Croatian Geological Survey, Zagreb, 1989.

[22] HRN EN ISO 5667-5:2000/2011 Water quality - Sampling-Part 5; Guidance on sampling of drinking water from treatment works and piped distribution systems (ISO 5667-5:2006)

[23] HRN EN ISO 15586:2008 en pr, Water quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace (ISO 15586:2003; EN ISO 15586:2003)

[24] Halamić, S. Miko, Z. Peh, E. Prohić, L. Galović, M. Šparica, *Geokemijsko kartiranje u Hrvatskoj - današnje stanje*, II Hrvatski geološki kongres. Cavtat-Dubrovnik, (2000), 27-32.

[25] J. Halamić, Z. Peh, *Geochemical Atlas of the Republic Croatia. Regional Spatial distribution of Arsenic*, Croatian Geological Survey, Zagreb, 2009, 34-35.

[26] K. Lozo, *Utjecaj crpljenja ugljikovodika na onečišćenje tala kadmijem, živom i arsenom. Diplomski rad*, Agronomski fakultet Sveučilišta u Zagrebu. Zagreb, 2015, 43.

[27] I. Kisić, *Sanacija onečišćenog tla. Udžbenici Sveučilišta u Zagrebu*, Zagreb, 2012.

[28] V. Novosel, *Onečišćenost tala arsenom na području Panonskog dijela Republike Hrvatske. Završni rad na specijalističkom sveučilišnom poslijediplomskom studiju Ekoinženjerstvo. Fakultet kemijskog inženjerstva i tehnologije*. Zagreb, 2008, 51.

[29] S. Žužul, Ž. Zgorelec, F. Bašić, I. Kisić, M. Mesić, V. Vadić, T. Ocr, *Arsenic in Air and Soil in the Vicinity of the Central Gas Station Molve, Croatia, Bulletin of Environmental Contamination and Toxicology*, 86/5, 501–505, 2011.

[30] F. Basic, *The Soils of Croatia*. World Soils Book Series. Springer. 2013, 179.

[31] <http://povijest.net/poplave-rijeke-drave-odredivale-su-zivotne-sudbine-podravaca/> (date of access: September 1st 2016)

[32] J. Skála, R. Vácha, J. Čechmánková, *Evaluation of arsenic occurrence in agricultural soils of the Bohemian Forest region, Silva Gabreta*, 2011, 17/2-3: 55-67.

[33] G. Tóth, T. Hermann, Da Silva M.R., L. Montanarella, *Heavy metals in agricultural soils of the European Union with implications for food safety*, *Environment International*, 88, 299-309, 2016.

[34] Regulation about the parameters of assessment and methods of analysis of water for human consumption. Official Gazette, 2013, 125.

[35] B.K. Thakur, V. Gupta, Arsenic concentration in drinking water of Bihar: health issues and socio-economic problems,

Journal of Water Sanitation and Hygiene for Development, 6, 2, 2016, 331-341.

[36] C.L. Chen, H.Y. Chiou, L.I. Hsu, Y.M. Hsueh, M.M. Wu, Y.H. Wang, C.J. Chen, Arsenic in drinking water and risk urinary tract cancer: a follow up study from Northeastern Taiwan, Cancer Epidemiology Biomarkers&Prevention, 2010, 19, 101.