# Analysis of arsenic monitoring in underground water of the Republic of Serbia for 2018-2020

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#### INTRODUCTION

Arsenic is a heavy metalloid that occurs frequently in nature. It can be found in the atmosphere, soil, rocks, natural waterways and organisms, but arsenic with the most effect on human health is in drinking water. World Health Organization (WHO) gave the recommendation for the maximum allowed concentration (MAC) of arsenic in the drinking water - $10 \mu g/I$ . This recommendation is adopted and included in the local legislative regarding hygiene of the drinking water in the public water systems, the Ordinance on the Hygiene of Drinking Water (Official Gazette of the FRY No. 42/98 and 44/99, Official Gazette RS No. 28/19).

Arsenic, can get into the environment in two ways: through natural processes (biological activity, rocks dissolution and volcanic emissions) and by anthropogenic activity (mining, production and use of pesticide, herbicide and wooden preservatives that contain arsenic, the arsenic use in livestock additives, draining crops, burning of fuel, deposition from the atmosphere, releasing waste water from industry and others) (Mason, 1966; Mason & Berry, 1978). Mining,

Arsenic is a heavy metalloid that occurs frequently in nature. The most serious repercussions for human health occur when it is found in drinking water (It can harm the circulatory, pulmonary, and nervous systems, as well as cause skin and other organs cancer). This paper presents the values of arsenic concentration in the Republic of Serbia's groundwater from 2018 to 2020, based on lab tests completed by the Serbian Environmental Protection Agency. Bearing in mind the fact that the Decree on Limit Values of Pollutants in Surface and Groundwater and Sediment and Deadlines for Reaching Them (Official Gazette of RS No. 50/12) does not prescribe limit values for arsenic in groundwater, as well as the fact that 75% of drinking water is supplied from groundwater, the results of testing the concentration of arsenic in groundwater are compared with the maximum allowed concentration of arsenic in drinking water prescribed by the Ordinance on the Hygiene of Drinking Water (Official Gazette of the FRY No. 42/98 and 44/99, Official Gazette RS No. 28/19). The concentrations of arsenic in eight piezometers were found to be above the maximum allowed concentration limit for drinking water for all three years. Having in mind the stated facts, it is necessary to update the regulations of the Republic of Serbia concerning the limit values of pollutants in groundwater, and to include the limit values for arsenic in it. The amendment of the regulation requires more detailed research regarding the concentration and origin of arsenic in groundwater.

> firstly gold mining and primary metals, is a branch of economy that contributes the most to polluting the groundwaters with arsenic, while burning coal is considered the most important anthropogenic pollution source for surface waters (Rahman & Husegawa, 2012).

> Arsenic can get in the human organism through water and food. But, when it is found in the human body, it can make many harmful effects on the health, including changes on the skin, influence the circulatory, pulmonary and nervous system, skin cancer and other organs. Symptoms of acute arsenic exposure include gastrointestinal problems, vomiting, diarrhea, anuria, convulsions, coma and death. Adults have a lethal dose estimated at 1-3 mg of As per kg of body weight (Markovski, 2014). International Agency for Researching Cancer (IARC) stated that As and its inorganic compounds are cancerous for humans (Group 1). Chronic exposure to arsenic includes skin, lung, liver and internal organ cancer (Jane, 2014). There are numerous data about the connection between cancer and drinking water with higher concentration of arsenic, but the risk for low concentrations of arsenic in the water has still not been assessed (Jovanović et al., 2011)

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## MATERIALS AND METHODS

Primary and secondary data were used in this paper, as well as both qualitative and quantitative data analysis. The materials used in this research - primary data, are official data from the Report on the Results of Surface and Underground Water Quality Tests, issued by the Environmental Protection Agency - Ministry of Environmental Protection. Also, data on reference values and limit values from the report of the World Health Organization, as well as valid national and EU regulations in the field of groundwater, were used as primary data. In addition, secondary data which was used represent the results of research conducted by other researchers and it was taken from the mentioned literature.

In order to define the reference value, which will be used to compare the measured values of arsenic concentrations in groundwater, the analysis of the relevant regulation and the defined limit values in it was primarily approached. After that, the quantitative analysis of primary data was applied, and the measured values of arsenic concentration in groundwater in the territory of the Republic of Serbia were compared with each other and with the defined reference limit. Quantitative analysis of primary data gave some results that are the basis for the final conclusions of this paper.

Secondary data from previous research by other authors was used in order to support the work with a qualitative approach and refer to potential problems that cannot be seen solely through quantitative analysis of primary data. Therefore, secondary data on measured arsenic concentrations in the soils of Vojvodina were used.

Data on the concentration of arsenic in waters on the territory of the Republic of Serbia, which are presented in the Reports on the results of surface and underground water quality tests, issued by the Environmental Protection Agency - Ministry of Environmental Protection, were determined by the method of induced-coupled plasma-mass spectrometry according to the standard EPA 6020 A : 2007 and EPA 6020 A : 2014.

# **RESULTS AND DISCUSSION**

Based on the Regulation of Determination of the Yearly Program of Monitoring Water Status for 2018 (Official Gazette RS, no. 35/18), Regulation of Determination of the Yearly Program of Monitoring Water Status for 2019 (Official Gazette RS, no. 45/19), Regulation of Determination of the Yearly Program of Monitoring Water Status for 2020 (Official Gazette RS, no. 85/20) and Regulation of Determination of the Yearly Program of Monitoring Water Status for 2021 (Official Gazette RS, no. 34/21) Serbian Environmental Protection Agency did a quality analysis of the groundwaters for the period 2018 - 2021. During 2018 and 2019 the analysis were performed on 53 piezometers, and during 2020 the analysis were performed on 54 piezometers. The results of the monitoring were published in the Reports on Results of the Surface and Groundwater Quality Analysis for 2018 (Denić et al., 2019), 2019 (Denić et al., 2020) and 2020 (Denić et al., 2021) issued by the Serbian Environmental Protection Agency - Ministry of Environmental Protection. The Regulation of Determination of the Yearly Program of Monitoring Water Status for 2021 prescribed the monitoring of groundwater on 57 piezometers, but until this moment the results haven't been published.

Limit values of pollutants in groundwaters of the Republic of Serbia is determined by the Decree on Limit Values of Pollutants in Surface and Groundwater and Sediment and Deadlines for Reaching Them (Official Gazette RS, No. 50/12). However, the mentioned Regulation did not define the limit values for arsenic. Also, the Directive on Protection of Underground Waters from Pollution and Decaying 2006/118/EZ of the European Parliament and Council from 12<sup>th</sup> of December 2006, didn't prescribed the limit values of arsenic in groundwaters, because arsenic can be found naturally as a result of hydrogeological conditions, so it's necessary for every country to regulate it's own limit values.

In the Republic of Croatia, the Regulation on Quality Standard of Water (Official Gazette RC, No. 96/2019) defined the limit values of arsenic in groundwaters, except mineral and geothermal waters. The defined limit value was 10 µg/l, which means that the limit values for arsenic in groundwaters is in complience with the World Health Organization (WHO) recommendation on the maximum allowed limit of arsenic in drinking water. In the mentioned regulation it is also stated that the limit values for arsenic of 10  $\mu$ g/l is not addressed to groundwaters that have high arsenic concentrations from their geological origin, but higher limit values are prescribed for the mentioned areas (Eastern Slavonia basin of Drava and Danube (500 µg/l), Eastern Slavonia basin of the Sava (250 µg/l), Legrad - Slatina (35 µg/l), Lekenik - Lužani (12 μg/l), Lonja – Ilova – Pakra (60 μg/l)).

In Republic of Serbia, the share of groundwater in public supply is around 75 % (Polomčić et al., 2011). The recommendation of WHO is that the maximum allowed concentration of arsenic in the drinking water must not exceed 10  $\mu$ g/l. In Serbia, the recommendation of WHO is accepted and implemented in the regulative Ordinance on the Hygiene of Drinking Water (Official Gazette FYR No. 42/98 and 44/99, Official Gazette RS No. 28/19) and it state that maximum allowed concentration (MAC) of arsenic in drinking water is 10  $\mu$ g/l.

Name of piezometer	Concentration As (μg/l)				Concentration As (µg/l)		
	2018	2019	2020	Name of piezometer	2018	2019	2020
Borča-dubok	/	1.7	4.9	Burza	/	3.0	2.6
Negotin	1.4	0.8	1.1	Kikinda	124.0	213.3	501.2
Negotin	1.4	0.8	0.9	Padej	71.4	122.7	109.1
Kusić	2.7	1.7	3.6	Bač	16.4	26.4	24.1
B.Karlovac	46.7	6.1	2.8	Nadalj	1.8	0.8	1.2
Sečanj	6.5	87.2	6.8	Novi Sad	1.8	1.1	1.1
Debeljača	1.0	1.5	37.9	Zrenjanin	1.7	2.5	2.1
Kovin	22.2	143.9	14.9	Bogatić	<0.5	/	4.8
Sombor	2.4	2.0	2.0	Bogatić	<0.5	/	0.6
Aleksa Šantić	14.4	12.3	7.4	Duvanište	<0.5	0.5	1.2
Njegoševo	3.7	2.0	1.3	Noćaj	1.6	3.9	3.3
Subotica-Milkićevo	70.2	31.8	21.8	Obrenovac	2.8	3.5	1.7
B. Aranđelovo	173.3	157.9	151	Zabrežje-Savksa 22	<0.5	0.6	0.8
Kanjiža	/	42.7	45.2	Laćarak	1.0	1.1	2.5
Vrbas-farma	4.1	5.2	4.8	Šid	5.8	0.6	2.4

Table 1. Measured concentrations of the arsenic (As) in groundwaters of Republic Serbia for the period 2018-2020

Table 2. Measured concentrations of the arsenic (As) in groundwaters of Republic Serbia for the period 2018-2020

Name of piezometer	Concentration As (µg/l)				Concentration As (µg/l)		
	2018	2019	2020	Name of plezometer	2018	2019	2020
Nikinci	0.7	10.9	12.5	Obrež – Ratare	5.0	10.1	3.0
Badovinci	<0.5	0.7	0.5	Varvarin – Ćićevac	3.6	1.3	1.9
Loznica-polje	0.8	0.7	1.3	Tobolac – Trstenik	8.3	11.6	9.8
Obrenovac-Beopetrol	<0.5	<0.5	1.6	Kruševac	1.5	2.1	2.1
Zvizdar	<0.5	1.2	1.6	Sirča (viseći most)	24.9	15.4	15.0
Čemanov most – Jabuka	/	<0.5	0.7	Stančići – seli	1.5	1.6	2.5
Bogovađa	0.7	0.5	1.1	Doljevačka petlja	2.1	1.8	1.5
Valjevo - GMS	0.9	3.2	1.3	Leskovac	3.7	3.5	3.4
Dubravica – Lipe	3.6	/	2.5	Leskovac	3.6	3.5	2.3
Lozovnik – Vlaški Do	3.4	4.4	4.2	Brzi Brod – selo	0.7	1.0	0.5
Šalinac	1.1	1.9	1.4	Žitkovac – ciglana	6.3	5.7	3.2
Markovac – Svilajnac	2.0	1.6	2.5	Žitorađa	5.2	7.1	2.7
Požarevac	1.5	1.3	2.6				
V. Plana- Žabari	17.5	12.6	11.8				
Bukovče – Glogovac	2.4	2.3	2.6				

Bearing in mind the fact that more than 2/3 of the population of Serbia is supplied with drinking water from underground water sources, the results of testing of the concentration of arsenic in underground water carried out by the Environmental Protection Agency during the subject three years (2018, 2019 and 2020), were compared with the maximum allowed concentration of arsenic in water for drink prescribed by the Ordinance on the Hygiene of Drinking Water, which is 10  $\mu$ g/l.

Analyzing the results and the issued limits, it has been detected that the concentration on arsenic during 2018 were above the maximum allowed concentration (MAC) on 10 piezometers in Republic of Serbia, namely: B. Aranđelovo, Kikinda, Padej, Subotica -Mikićevo, Sirča - viseći most, B. Karlovac, Kovin, B. Plana - Žabari, Bač, Aleksa Šantić. During the 2019 on 14 piezometers MAC exceeding was detected on following locations: Kikinda, B. Arandelovo, Kovin, Padej, B. Karlovac, Kanjiža, Subotica - Mikićevo, Bač, Sirča - viseći most, Aleksa Šantić, Tobolac - S.Trstenik. When it comes to 2020 arsenic concentration was exceeding the maximum allowed concentration on 11 piezometers in: Kikinda, B. Aranđelovo, Padej, Kanjiža, Debeljača, Bač, Subotica - Mikićevo, Sirča - viseći most, Kovin, Nikinci, V. Plana - Žabari).

Data analysis revealed that arsenic concentrations on 8 piezometers exceeded the prescribed MAC in drinking water during all three subject years, as shown in the Figure 1. The highest measured concentration of As in groundwater was detected at the Kikinda piezometer during 2020, and was 501,2  $\mu$ g/l. Also, it was established that the concentration of arsenic measured at this piezometer increases from year to year and in three years it increased from 124  $\mu$ g/l to 501,2  $\mu$ g/l.



Figure 1. Display of the measured concentrations of arsenic in groundwater at the eight piezometers on which exceeds were detected

From the analysis of the presented data it is detected that out of the eight piezometers where a constant exceedance was detected in the three subject years, six are located in the territory of the Autonomous Province of Vojvodina. The geographic location of the piezometers where the concentration of As was exceeded MAC during the whole period of three years is shown in the Figure 2.



Figure 2. The geographical position of piezometers which had As concentration over the MAC during 2018-2020

Based on the fact that on the concentration of arsenic in groundwater is affected by geological, geomorphological and hydrogeological characteristics of the area, it's assumed that the deep permable sediments from the middle and upper pleistocene contain As minerals, most common arsenopirit FeAsS, isomorphous mixture  $FeS_2$  and  $FeAs_2$ , and that they represent sources of As in the groundwaters of Vojvodina (Marinković et al., 2007, Ujević et al., 2010). Based on data (Jovanović et al., 2011) in Vojvodina the concentration of arsenic in tercial magmatic rocks was 3,1 mg As/kg while its concentration in the soil was 10 mg As/kg.

Figure 3 shows the mean concentrations of arsenic at eight piezometers where MAC was exceeded during all three subject years. The graph shows that the highest mean concentration of As measured over three years was 279.5  $\mu$ g/l, detected at the Kikinda piezometer. At the piezometer in B. Arandjelovo, a mean value of 160.73  $\mu$ g/l was measured, which is 16 times higher than the maximum allowed concentration of MAC in drinking water.



Figure 3. Mean concentrations of As at the piezometers where the MAC was exceeded in the subject period

Taking into account the mentioned above, arises the question of the necessity of defining limit values of polluting substances, specifically arsenic in groundwater, that is, the need to amend and supplement the existing regulations in this area. Therefore, it would be necessary to carry out detailed research regarding the concentration and origin of arsenic in groundwater, in order to define the areas of the Republic of Serbia whose groundwater naturally contains high concentrations of arsenic.

#### CONCLUSION

In this paper, the results of the investigation of the concentration of arsenic in groundwater carried out by the Environmental Protection Agency during the period 2018-2020 were compared with the limit values prescribed by the Ordinance on the Hygiene of Drinking Water (Official Gazette FYR No. 42/98 and 44/99, Official Gazette RS No. 28/19). The aforementioned comparison was made considering the fact that more than 75% of the population of Serbia is supplied with drinking water from underground sources, as well as that the Regulation on Limit Values of Pollutants in Surface and Underground Waters and Sediment and the Deadlines for Their Achievement (Official Gazette of the RS, No. 50/12), have not defined limit values for arsenic (As).

It was concluded that the concentrations of arsenic on eight piezometers, of which even six are located on the territory of Vojvodina, were above the prescribed MAC in drinking water during all three investigated years. On the basis of the above, as well as the fact that Directive 2006/118/EC of the European Parliament and the Council of December 12, 2006, on the protection of groundwater from pollution and degradation, states that each country should prescribe its own limit values because arsenic can be naturally present in waters as a consequence of hydrogeological conditions, it was concluded that there is a need for changes of the Regulation on Limit Values of Pollutants in Surface and Underground Waters and Sediment and the Deadlines for Their Achievement. It is necessary to prescribe a limit value for arsenic in groundwater, as well as to additionally examine and define the areas of the Republic of Serbia whose groundwater naturally contains high concentrations of arsenic, and to which the prescribed limit value will not apply.

## REFERENCES

- Chatterjee, S., & De, S. (2017). Adsorptive removal of arsenic from groundwater using chemically treated iron ore slime incorporated mixed matrix hollow fiber membrane. *Separation and Purification Technology*, 179, 357-368. <u>https://</u> doi.org/10.1016/j.seppur.2017.02.019
- Denić, Lj., Stojanović, Z., Dopuđa-Glišić, T., Čađo, S., Đurković, A., Novaković, B., & Domanović, M. (2019). Agencija za zaštitu životne sredine Republike Srbije, Ministarstvo zaštite životne sredine, <u>http://www.sepa.gov.rs/download/</u> vode\_godisnji\_2018.pdf
- Denić, Lj., Stojanović, Z., Dopuđa-Glišić, T., Čađo, S., Đurković, A., & Novaković, B. (2020). Agencija za zaštitu životne sredine Republike Srbije, Ministarstvo zaštite životne sredine, <u>http://www.sepa.gov.rs/download/</u> <u>KvalitetVoda\_2019.pdf</u>
- Denić, Lj., Stojanović, Z., Dopuđa-Glišić, T., Čađo, S., Đurković, A., & Novaković, B. (2021). Agencija za zaštitu životne sredine Republike Srbije, Ministarstvo zaštite životne sredine, <u>http://www.sepa.gov.rs/download/</u> KvalitetVoda\_2020.pdf
- Hung, D., Nekrassova, O., & Compton, R. (2004). Analytical methods for inorganic arsenic in water: a review. *Talanta*, 64(2), 269-277. <u>https://</u> doi.org/10.1016/j.talanta.2004.01.027
- Jane, M. (2014). Arsenic: Detection, Management Strategies and Health Effects. Nova Science Publishers.
- Jovanović, D., Jakovljević, B., Rašić-Milutinović, Z., Paunović, K., Peković, G., & Knežević, T. (2011). Arsenic occurrence in drinking water supply systems in ten municipalities in Vojvodina Region, Serbia. *Environmental Research*, 111(2), 315-318. <u>https://doi.org/10.1016/j.</u> envres.2010.11.014
- Marinković, D., Vidović, M., Maldenović, N., & Tomić, I. (2007). Uklanjanje arsena iz podzemnih voda sa područja Zapadnobačkog okruga [Elimination of Arsenic from the Underground Waters in the Region of West Bačka]. Proceedings – international Scientific

Meeting "The seventh international conference Water Supply and Sewerage Systems". (pp. 176-186). Jahorina – Pale.

- Markovski, S. J. (2014). Separation of arsenic from water using natural and solvothermally synthesized calcite modified by metal oxides (Doctoral disseration). https://nardus.mpn.gov.rs/bitstream/ handle/123456789/6371/Disertacija4350.pdf
- Mason, B., & Berry, L. (1978). Elements of Mineralogy. Freeman.
- Mason, B. (1966). Principles of Geochemistry, McGraw-Hill.
- Mohan, D., & Pittman, U. (2007). Arsenic removal from water/wastewater usingadsorbents - A critical review. *Journal of Hazardous Materials*, 142, 1-53. <u>https://doi.org/10.1016/j.</u> jhazmat.2007.01.006
- Polomčić, D., Stefanović, Z., Dokmanović, P., Papić P., Ristić Vakanjac, V., Hajdin, B., Milanović, S., & Bajić, D. (2011). Vodosnabdevanje i odživo upravljanje podzemnim vodnim resursima u Srbiji podzemnim vodama u Srbiji, *Vodoprivreda*, 44, 225-231. <u>https://doi. org/10.5772/33403</u>
- Rahman, M., & Hasegawa, H. (2012). Arsenic in freshwater systems: Influence of eutrophication on occurrence, distribution, speciation and bioaccumulation. *Applied Geochemistry*, 27(1), 304-314. <u>https://doi. org/10.1016/j.apgeochem.2011.09.020</u>
- Ujević, M., Duić, Ž., Casiot, C., Sipos, L., Santo, V., Dadić, Ž., & Halamić, J. (2010). Occurrence and geochemistry of arsenic in the groundwater of Eastern Croatia, *Applied Geochemistry*, 25(7), 1017-1029. <u>https://doi.org/10.1016/j.</u> <u>apgeochem.2010.04.008</u>