MGPB

Rudarsko-geološko-naftni zbornik

The Mining-Geological-Petroleum Engineering Bulletin

Godište XXXIII., broj 56 / Anno XXXIII, number 56

Editorial Team

Editorial board

MGPB

Radovi/*Papers*

eISSN 1849-0409

9 770353 452009

Godište XXXIII., broj 56 / Anno XXXIII, number 56

MGPB

Rudarsko-geološko-naftni zbornik
(The Mining-Geology-Petroleum Engineering Bulletin)
UDC: 622.8
DOI: 10.17794/rgn.2021.5.11

Preliminary communication

Pollution with Cr^{6+} of Groundwater and Surface Water from the Industrial Dump Jugohrom - Jegunovce – the Republic of North Macedonia

Stojan Mihailovski[1]; Vojo Mircovski[2]; Zlatko Ilijovski[1]

[1] *Civil Engineering Institute "Macedonia" JSC Skopje, the Republic of North Macedonia info@gim.com.mk*

[2] *Faculty of Natural and Technical Sciences, Institute of Geology, "Goce Delcev" University in Stip Str. Goce Delcev 89, 2000 Stip, the Republic of North Macedonia.*

Abstract

In order to investigate the pollution with hexavalent chromium (Cr^{6+}) of the groundwater and surface water around the industrial dump Jugohrom – Jegunovce, hydrogeological investigations were carried out during November 2019, where 16 samples of groundwater and 3 samples of surface water were taken. In most of the analyzed samples of groundwater and surface water, the concentration of Cr^{6+} exceeds the maximal allowed concentrations (MAC) of Cr^{6+} (0.01 mg/l) according to the Macedonian and European standards in drinking water. The highest contamination with Cr^{6+} which is in the range of 0.052 – 132.98 mg/l is registered near the dump in the shallow groundwater, i.e. in the unconfined aquifers. Cr^{6+} pollution ranging from 0.017 to 0.041 mg/l has also been registered in some of the samples at artesian aquifers with a sub-artesian level. Two tests were carried out on the surface water of the Vardar River, before and after the dump. A sevenfold increase in Cr^{6+} concentration of 0.069 was observed after the dump. Cr^{6+} content of 725 mg/l was found in the drainage of overflow water in the discharge. Pollution of the groundwater and surface water with Cr^{6+} is anthropogenic and is a result of the operation of the Metallurgical Plant Jugohrom in the period from 1955 to 1994.

Keywords:

hexavalent chromium Cr^{6+}; groundwater; pollution; Zheden; Rashche Spring

1. Introduction

The industrial dump Jugohrom is located in the north-east part of the Polog Valley, at a distance of about 30 km from the city of Skopje, in the recharge zone of the Rashche Spring. East of the dump, at about 100 m, the carbonate Zheden Massif begins, in which there is a karst aquifer which is a recharge zone for the Rashche Spring.

Some authors point out that chromium contamination of the surface and groundwater is a serious environmental problem in many European Union countries (**Tumalo et al., 2020**). Among the possible forms of chromium, hexavalent is the most toxic (**Pellerin et al., 2000**). It causes liver and kidney damage, internal bleeding, and respiratory disorders. It has been identified as a carcinogen for humans (Group I) by the International Agency for Cancer Research (**Lyon, 2012**). It can enter the human body when they breathe air, eat food or drink water containing Cr^{6+} (**De Flora et al., 1989**).

The most well-known and widely used method of purifying polluted water is the reduction of Cr^{6+} into a less mobile and less toxic form of Cr^{3+}, using a variety of agents in an acidic environment. Cr^{6+} remediation strategies include physical-chemical and biological methods (**Koleli et al., 2016**).

High concentrations of Cr^{6+} (> 0.05 mg/l) were detected in the groundwater in Eastern Sterea Hellas (central Euboea and Asopos Valley) in Greece (**Vatilatos et al., 2010**). A total of 16 groundwater samples were taken for analysis from both areas (9 from central Euboea and 7 from Asopos Valley). Groundwater pollution with Cr^{6+} at central Euboea was mainly related to natural processes, but there were cases when it was also associated with anthropogenic activities. In the Asopos Valley area, Cr^{6+} contamination was associated with industrial waste.

Cr^{6+} contamination has been detected in most water wells in the Thiva - Tanagra - Malakasa Nasin area, Greece (**Vasilatos et al., 2008**). During the realization of these investigations, a total of 63 samples of surface water and groundwater were taken. High concentrations were found in the urban water supply system of Oropos (up to 80 µg/l Cr^{6+}) and Inofyta (up to 53 µg/l Cr^{6+}). The source of pollution is associated with widespread industrial activity and the use of Cr^{6+} in various processes and wastewater discharge in the past 40 years.

Rashche is a karst spring with a yield ranging from 3.18 to 9.6 m^3/s, average 5.15 m^3/s (Data from Vodovod

Corresponding author: Stojan Mihailovski
stojan.mihailovski@gim.com.mk

- Skopje 2007 to 2015). The spring is characterized by high consistency in capacity and stable and good water quality. About 92% of the population numbering about 600000 inhabitants from the Skopje region and most of the economy meets the water needs from this source.

In the past period, several investigations have been done in R. N. Macedonia that describe the geology and hydrogeology of Polog Valley, including the terrain around the industrial dump Jugohrom, and some of them refer to the Cr^{6+} contamination of the groundwater and surface waters around the dump. (**Kekić, 1986; Radovanović et al., 1989**).

The industrial dump was established as a result of the production process of the plant in the period from 1955 to 2016 by the Metallurgical Plant Jugohrom from Jegunovce. The dump covers an area of about 7 ha, with an average height of about 23 m. The dump contains about 1200000 m^3 of various waste: metallurgical slag, construction waste, municipal waste from the factory and surrounding settlements and bichromatic swamp. The bichromatic swamp was produced as a by-product in the period from 1955 to 1994, and it has a quantity of 350000 t. It contains Na_2CrO_4 2.1%, of which 0.7% in the form of Cr^{6+}, and the content of Cr_2O_3 is 5%.

In the past period, extensive investigations were conducted and technical solutions were made for remediation of the harmful impacts from the dump by diversion of the surface waters, construction of drainage systems for the intake of contaminated shallow groundwater and seepage water with Cr^{6+} under the dump and their pumping and purification in the treatment plant in the Metallurgical Plant Jugohrom, (**Soro et al. 2001**).

The current actual problem is that the constructed drainage system and the pumping station for receiving and treating the shallow drain and contaminated waters from the dump work periodically, and only partially fulfilling the aim for what they are intended. As a result of the incomplete function of the drainage system and the pump station, the drain contaminated waters, including the high content of Cr^{6+}, spill from the drainage and directly overflow in the Vardar River and the shallow groundwater, **Figure 1**. As a result of this condition, the river water, downstream of the dump shows increased concentrations of Cr^{6+}. On this part of the terrain and downstream, the Vardar River directly communicates with the carbonate Zheden Massif. On the other hand, with previous research it has been proven that the Vardar River partially charges the Zheden Massif and the Rashche Spring (**Kekić, 1986**).

The previous investigations for the pollution with Cr^{6+} referred to the shallow groundwater in the unconfined aquifer, located directly under the dump and exposed to the largest direct infiltration from the dump and the contaminated soils around the Metallurgical Plant. In the period from 2010-2015, the Metallurgical Plant (Archive of "Silmak" or former "Jugohrom") conducted monitored of the Metallurgical Plant and the industrial

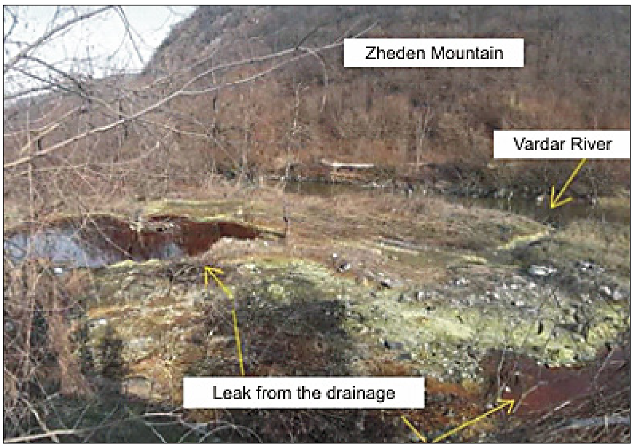


Figure 1: Drainage discharge, 2019

dump to determine the content of Cr^{6+} in groundwater and surface water. With this monitoring, the presence of Cr^{6+} above MAC (> 0.01 mg/l) was detected. In the vicinity of the plant, the content of Cr^{6+} was in the range of 0.21 – 14.23 mg/l, while in the vicinity of the dump, the concentrations with Cr^{6+} was higher and the content was in the range of 0.03 – 1751.30 mg/l.

In the period before the start of the process of depositing the waste material, a concrete pipe Ø 1000 mm was installed under the present dump, which in the beginning was transferring the water from the creek Muzga, located above the dump towards the Vardar River. This concrete channel was damaged and the contaminated water from the dump leaked in it. Also, during heavy precipitation this channel could not receive the entire volume of water from the creek. Therefore, before the dump, another concrete channel Ø 2000 mm was additionally constructed for redirecting the water from the creek Muzga outside of the dump. In the old concrete pipe Ø 1000 mm, now a PVC pipe of Ø300 mm and a steel pipe Ø 3/4" have been installed, and the last 30 m are sealed with concrete (see **Figure 2**). The PVC pipe Ø 300 mm is for conducting the groundwater from the drainage above the dump to the Vardar River, and the steel pipe Ø 3/4" intakes the drain contaminated water from the dump, entering through the damaged parts of the concrete pipe.

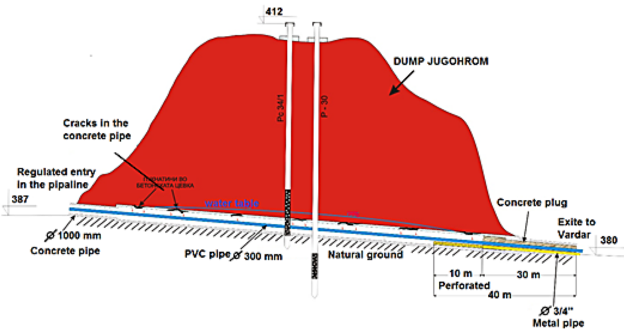
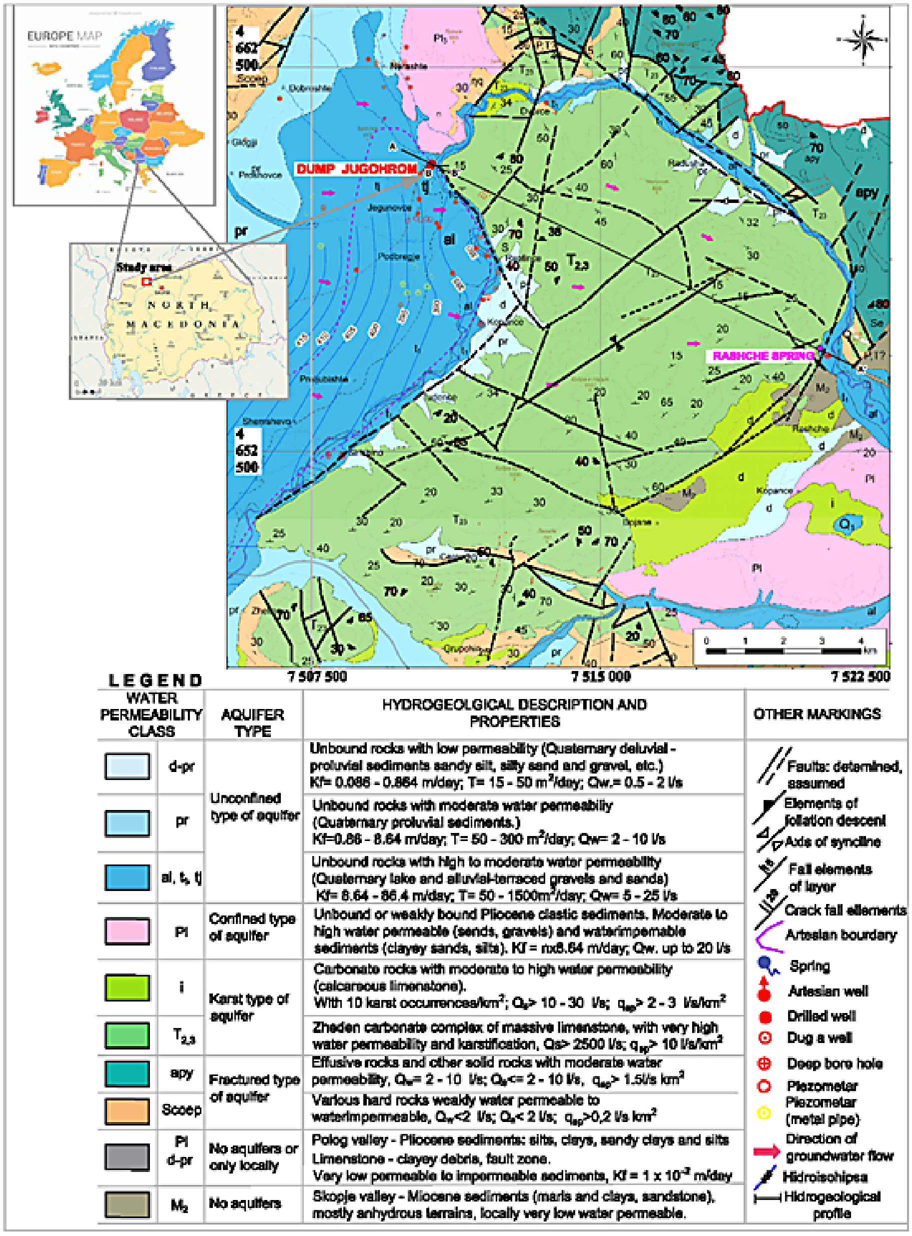


Figure 2: Schematic representation of pipeline under the dump



* The legend refers to Figure 3, 4 and 6

Figure 3: Hydrogeological map of the wider area of the investigated terrain

The last investigations, realized during 2019, were conducted to determine the groundwater quality, and the impacts of the dump on the unconfined aquifer, as well as the deeper confined aquifers with sub-artesian level. Piezometers were installed which separately intake water from both aquifers. The direct contact zone (tectonic contact-fault) of the unbound sediments from the Polog Basin and the carbonate massif near the dump were also investigated (**Ilijovski et al., 2019**). This zone is of large importance for the movement of groundwater from the unbound sediments of Dolen Polog which are contaminated, towards the carbonate complex Zheden in the direction of the groundwater towards the Rashche Spring. These investigations have determined in more details the hydrogeological characteristics of the area between the dump and the carbonate Zheden Massif. The results obtained from these investigations are presented in this paper.

2. Geology

Based on the geo-tectonic regionalization of the R. N. Macedonia, the investigated terrain belongs to the western Macedonian zone, and is part of the extreme northeastern part of the Polog Neotectonic Graben (**Arsovski, 1997**). The Polog Valley is a typical two-sided graben filled with Upper Miocene-Pliocene sediments represented by gravel - sandy and clayey sediments. These sediments in the area of Dolen Polog have a thickness up to 600 m. (**Dumurdzhanov, 1995, 2004, 2005 and 2008**).

Pliocene sediments on the surface are covered with Quaternary sediments, except on the stretch Jegunovce – Oreshje – Vratnica, where they are found on the surface. Quaternary sediments are represented by lake, fluvio-glacial, proluvial and alluvial sediments. The base of the Polog Valley and its peripheral mountainous parts are built of Paleozoic and Mesozoic rocks (**Petkovski et al., 1985**). Paleozoic rocks are mainly represented by green schists, chlorite-epidote-sericite-quartz schists, albite-chlorite-epidote-sericite and other schists, graphite schists, and from the eruptive rocks there are granites, which are usually schistose. Mesozoic rocks are mainly represented by: limestones, argiloschists, sandstones, dunnites, harzburgites, serpentinites and others. The sediment base is composed of metamorphosed diabase, Paleozoic schists and carbonate rocks. The industrial dump, which is the subject of the investigation in this paper, is located on the first river terrace of the river Vardar, i.e. at the entrance of the river Vardar in the Derven Gorge.

3. Hydrogeology

The hydrogeological structure of the wider area around the investigated site is shown on the Hydrogeological map, see **Figure 3** (**Ilijovski, 2013; Petkovski et al., 1985; Janchevski et al., 1982**). According to the structural type of porosity that occurs in the rocks represented in the wider area, the following types of aquifers can be distinguished:

- Unconfined type of aquifers,
- Confined type of aquifers,
- Karst type of aquifers,
- Fractured type of aquifers, and
- Terrains without aquifers.

Each aquifer is characterized with special characteristics and significance. Short description and hydrogeological parameters will be provided for each aquifer in the text below.

Unconfined type of aquifers is formed in the unbound sediments of the Polog Valley of tertiary and Quaternary age, which are characterized by intergranular porosity. Within these aquifers, according to the permeability and yield, the following types of aquifers can be distinguished:

- Aquifers with low water permeability and water bearing capacity,
- Aquifers with moderate water permeability,
- Aquifers with moderate to high water permeability and water bearing capacity.

Aquifers with low water permeability and water bearing capacity are formed in the clayey deluvial and proluvial sediments along the perimeters of the Polog Valley and in the limestone clayey debris that occurs in some fault zones along the perimeter of the valley, i.e. in the contact zone of the Zheden Massif with the Polog Valley. These aquifers have hydraulic conductivity Kf = 0.086 – 0.86 m/day, transmissibility coefficient T = 15 - 50 m^2/day and a well yield Qw. = 0.5 - 2 l/s.

- Aquifers with moderate water permeability

They are formed in the proluvial sediments composed of gravel and sand as well as clayey gravelly sediments that occur along the peripheral parts of the Polog Valley. They are characterized by hydraulic conductivity Kf = 0.86 – 8.64 m/day, transmissibility coefficient T = 50 - 300 m^2/day and a well yield Qw. = 2 – 10 l/s.

- Aquifers with moderate to high water permeability and water bearing capacity

These aquifers are formed in modern alluvial sediments and Quaternary lake and alluvial terraced sediments.

- *Modern alluvial sediments,* which are composed of various granular sands and gravels, in some places clayey ones occur along the river Vardar. They have hydraulic conductivity Kf = 8.64 – 86.4 m/day, a transmissibility coefficient of T= 30 – 1500 m^2/day and a well yield of Qw.= 10 – 25 l/s.

- *Quaternary - lake and alluvial terrace sediments* cover the entire Polog Valley to a depth of about 20 - 30 m. In these sediments, the change of lithological units is very common, both in horizontal and vertical profile, due to which there is a difference in the hydraulic conductivity. Generally, they are characterized by hydraulic conductivity Kf = 0.86 – 86.4 m/day, transmissibility coefficient T = 50 - 1500 m^2/day and a well yield Qw. = 5 - 25 l/s.

The movement of groundwater in the Polog Valley is in the general direction from the foot of Shar Mountain towards the river Vardar, as well as from Dolen Polog towards the carbonate Zheden Massif. Groundwater levels in the central and eastern parts of the valley are quite shallow and range from 2 - 5 m.

The confined type of aquifers with sub-artesian and artesian level. According to the hydrodynamic properties of the level in the northeastern parts of the Polog Valley in the complex of water-permeable and water-impermeable Upper Pliocene - lake sediments, ***aquifers with sub-artesian and artesian level*** have been formed. The depth at which the artesian aquifers occur is 20 - 100 m, with a hydraulic conductivity mainly in the range of Kf = 0.864 - 8.64 m/day and with a well yield of up to 20 l/s.

The karst type of aquifer is formed within the Triassic carbonate rocks of which the Zheden Massif is composed, located at the northeastern contact points with the Polog Valley**.** The Zheden karst aquifer is of exceptional importance due to the Rashche Spring, which discharge on the tectonic boundary between the Zheden Massif and the Skopje Valley (see **Figure 4**).

The Rashche Spring's discharge at an elevation 300, while the carbonate rocks of the Zheden Massif are characterized with intensive and deeper karstification, deep-

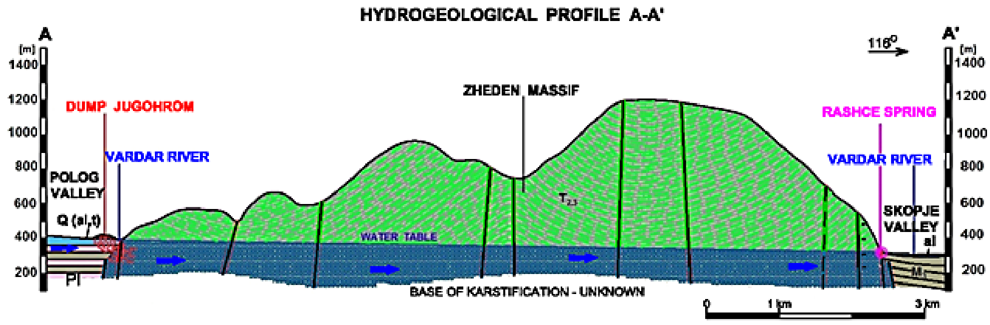


Figure 4: Hydrogeological profile of Polog Valley – Zheden Massif – Skopje Valley

er than elevation 300. The Zheden carbonate complex is characterized with very high water permeability and karstification, a spring yield Q_s >2500 l/s, module of groundwater leakage q_{sp} > 10 l/s/km^2. The abysses of Polog Valley near Raotince participate in the recharge of the Zheden Aquifer, especially in conditions of rising water levels of the Vardar River (**Kekić, 1986**).

The fracturing type of aquifers occur in the surrounding mountain massifs around the Polog Valley in the Paleozoic solid rocks which consist of the crystalline schists with lower crystallinity and the eruptive rocks which have low water permeability. The aquifers are represented only locally and shallow under the terrain surface, in depth these environments are arid, except along the tectonic-fault structures. The yield of the springs in these environments is usually lower than Q_s < 2 l/s, module of groundwater leakage q_{sp} = 0.2 l/s/km^2.

Terrains without aquifers are represented with Miocene sediments (marls, marl clays, sandstones). They are very low water permeable to water impermeable, mostly arid terrains. They are located in Skopje Basin and at the contact with the Zheden Massif, at the location of the Rashche Spring.

4. Methodology

During 2019, three piezometers (SP-1= 21 m depth, SP-2= 48 m and SP-3= 59 m) and 3 investigation wells (IB-1 = 23 m, IB-2= 65 m and IB-3= 55 m) were constructed, for more detailed defining of the hydrogeological characteristics between the industrial dump Jugohrom and the karst Zheden Massif.

During November 2019, from an aspect of the content of Cr^{6+}, a total of 19 samples were taken at once, 16 of which are from groundwater and 3 are from surface waters for determining the groundwater and surface waters contamination. Samples were taken from piezometers constructed 2019, as well as from existing piezometers. The location of the taken samples is shown in **Figure 5**, with ordinal numbers from 1 to 19.

For determining the Cr^{6+} content, in the groundwater the samples were taken from the piezometers and wells covering the waters from the unconfined aquifers, or the shallow waters occurring at a depth of about 23 m, SP-1

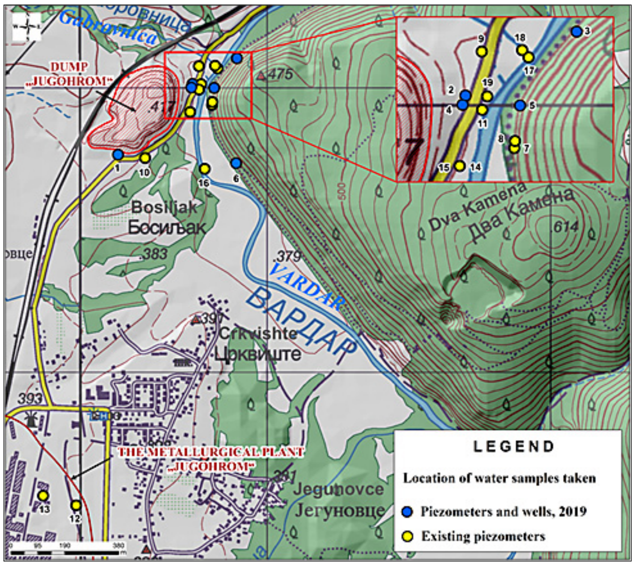


Figure 5: Location of water samples taken

(21 m), IB-1 (23 m), P-1 (6 m), P-19/2 (14.8 m), P-32/1 (5.5 m) and P-35/1 (6 m) and from the piezometers and wells covering the waters from the confined aquifers with sub-artesian level SP-2 (48 m), SP-3 (59 m), IB-2 (65 m), and P-2 (100 m), or the deeper waters occurring at a depth of about 100 m, the karst aquifer in the carbonate massif Zheden IB-3 (55 m), as well as from a pipe ø300 mm (**14**) and a pipe with a valve ø3/4" (**15**).

Only 2 samples were taken from the piezometers P-15/2 (7.5 m) and P-8 (20 m) in the area around the Plant Jugohrom. A total of 3 samples were taken from the surface waters from the Vardar River, before the dump (**17**) and after the dump (**18**), from the inflow of the river Gabrovnica in the Vardar River (**19**). A sample was taken also from the leachate occurring as drainage spillway (**16**).

The water samples were taken in plastic bottles which were previously well washed, and after they were analyzed in the Public Health Institute in Skopje by Flame atomic absorption spectrometry method (FAAS). 100 ml of water was taken from each sample into which 1 ml 65% HNO_3 acid was added. Then, each sample was treated with dry digestion on an electric hob. In the completely evaporated sample 10 ml 4% HNO_3 acid was added. The

Table 1: Limit values standards of total chromium (Cr) and hexavalent Cr^{6+}

	USEPA, 2008	EU, 1998	WHO, 2008	Iranian, 1997	Australian, 1996	Indian, 2005	New Zealand, 2008
Cr (µg/l)	100	50	50	50	50[c]	50[c]	50

[c] Chromium as Cr^{6+} not as total Cr

obtained measuring solution was used for determining the Cr^{6+} with atomic absorption spectrometry.

More countries, including the European Union have regulated the limited value for total chromium of 0.05 mg/l (**Directive 98/83/EC**). The maximal acceptable limit for Cr^{6+} in the drinking water has not been determined yet in the European Union and many other countries. Italy has regulated Cr^{6+} to 0.005 mg/l in drinking water (**Fantoni et al., 2020; Stepek, 2020**). Chromium as a contaminant in drinking waters has various values for the maximal allowed concentrations for different national and international organizations, shown in the following table (**Gebrekidon et al., 2011**).

The obtained results of the Cr^{6+} content in the analyzed samples of groundwater and surface waters are compared with the Macedonian standard for maximal allowed concentrations (MAC) of Cr^{6+}, which is 0.96 micromoles/l, or (0.01mg/l) in the drinking waters (**Official Gazette of R. M. no. 5/1984. Rulebook for the quality and health safety of drinking water**).

5. Results and discussion

With the construction of the investigation wells and piezometers, it is determined that in the zone between the dump and the contact with the Zheden Massif, there are aquifers in the unbound sediments, or there is an unconfined type of aquifer and confined types of aquifers with artesian and sub-artesian level and karst types of aquifers in the Zheden Massif. Based on testing the yield of IB-1 for the unconfined aquifer, the following is obtained: hydraulic conductivity Kf = 9.75 m/day and transmissibility coefficient T = 97.55 m^2/day. For the confined aquifer with sub-artesian level, based on testing of SP-1 the following is obtained: hydraulic conductivity Kf= 0.93 m/day and transmissibility coefficient T= 18.67 m^2/day. The groundwater level in this area is within 4 - 5 m.

Limestone-clayey debris, rather clayey with pieces of limestones is also registered on the contact between the unbound sediments and the Zheden Massif, with interlayers of clayey sand and sandy clays (tectonic contact-fault). They are very low water permeable to water impermeable sediments, poor aquifers to arid, with hydraulic conductivity Kf= $1x10^{-2}$ m/day, calculated based on the results from testing the yield of IB-2. The hydrogeological profile of the terrain between the industrial dump Jugohrom and the Zheden Massif is shown in **Figure 6.**

The obtained results from the Cr^{6+} content in the samples taken from the groundwater and the surface waters and how many times the concentration of Cr^{6+} has increased in relation to the maximal allowed concentrations (MAC = 0.01 mg/l) are shown in **Table 2.**

The contents of Cr^{6+} are shown graphically in **Figure 7**, and their comparison with MAC of Cr^{6+} (0.01mg/l) according to the Macedonian standard for drinking water. From the diagram it can be seen that increased concentration of Cr^{6+} are determined within a large number of samples in comparison to the MAC.

Based on the performed analyses and the spatial arrangement of the locations where the groundwater samples have been taken, it can be concluded that the highest contamination with Cr^{6+} in relation to MAC occurs near the dump, in the shallow groundwater, or in the unconfined aquifers. The Cr^{6+} content in these aquifers ranges between 0.052 – 132.98 mg/l. The highest concentrations of Cr^{6+} in the shallow groundwater are determined in the well IB-1 (23 m depth) with Cr^{6+} concentration Cr^{6+}=

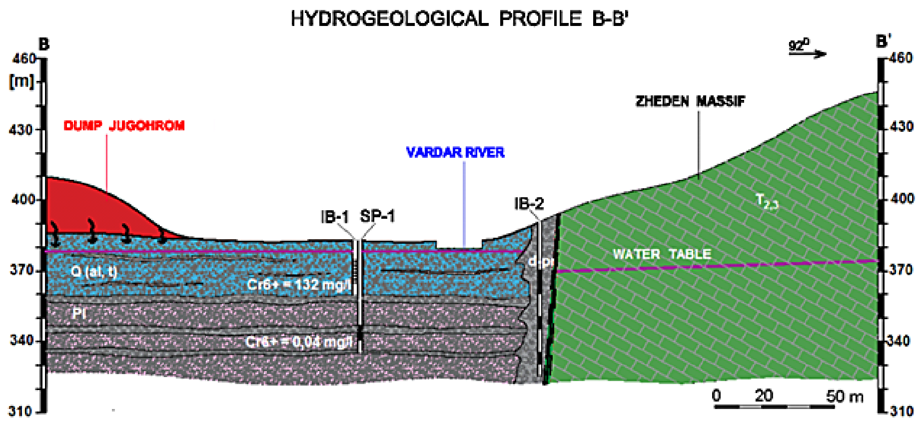


Figure 6: Hydrogeological profile of the location dump Jugohrom – Vardar River – Zheden Massif

Table 2: Cr^{6+} content in samples from groundwater and surface water in the surrounding environment of Jegunovce

	Sample Number	Location of taken sample	Depth (m)	Cr^{6+}(mg/l) Content	How many times has the concentration of Cr^{6+} increased in relation to MAC *
Groundwater	1	Piezometer SP-1, 2019	21	7.4	740
	2	Piezometer SP-2, 2019	48	0.041	4.1
	3	Piezometer SP-3, 2019	59	0.017	1.7
	4	Investigation well IB-1, 2019	23	132.98	13298
	5	Investigation well IB-2, 2019	65	n.d.	/
	6	Investigation well IB-3, 2019	55	n.d.	/
	7	Piezometer P-1	6	29.8	2980
	8	Piezometer P-2	100	0.018	1.8
	9	Piezometer P-19/2	14.8	n.d.	/
	10	Piezometer P-32/1	5.5	3.9	390
	11	Piezometer P-35/1	6	0.052	5.2
	12	Piezometer P-15/2	7.5	0.306	30.6
	13	Piezometer P-8	20	1.93	193
	14	PVC pipe ø300 mm	/	n.d.	/
	15	Pipe with valve ø3/4"	/	8.226	822.6
	16	Drainage spillway	/	725	72500
Surface water	17	Vardar River, before the dump	/	n.d.	/
	18	Vardar River, after the dump	/	0.069	6.9
	19	Gabrovnica River - influx in the Vardar River	/	n.d.	/

* Values greater than 0.01 mg/l are marked in red

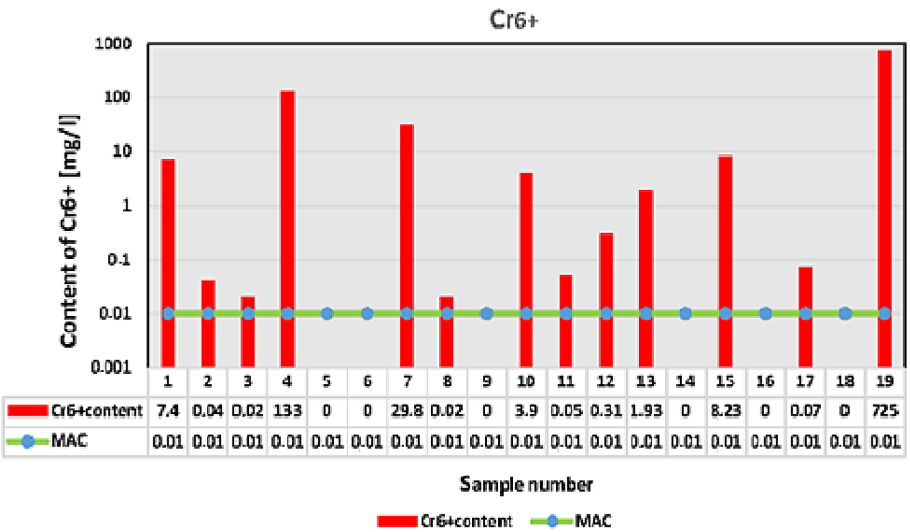


Figure 7: Graphic review of Cr^{6+} contents from taken water samples, 2019. MAC limit for Cr^{6+} is also shown

132.98 mg/l, or there is 13300 times higher concentration in relation to the MAC. This well is located under the dump in its vicinity (see **Figure 5**). Only in the piezometer with ordinal **no. 9**, which is at the greatest distance from the dump, Cr^{6+} has not been registered.

The concentration in the unconfined aquifer is visibly high, while in the confined aquifers with sub-artesian level, the concentrations are rather smaller. This is a result of the hydrogeology of the terrain. The Cr^{6+} content in these aquifers ranges between 0.017 – 0.041 mg/l and it is lower than the content of Cr^{6+} in the shallow groundwater.

In the investigation well marked with ordinal **no. 5** located at the contact with the Zheden Aquifer, content of Cr^{6+} has not been registered. This is also a result of the hydrogeology of the terrain. In the well IB-3 marked with ordinal **no. 6**, performed in the Zheden Massif, with karst type of aquifer, content of Cr^{6+} is not detected. Increased concentrations of Cr^{6+} occur also in the water sample **no. 15** taken from the pipe with valve ø3/4" going under the dump and intakes the drain contaminated water from the dump.

The enormously high concentration of Cr^{6+} (725 mg/l) 72500 times higher in relation to the allowed are determined in the water sample **no. 16** which is taken as spillway after from the drainage of contaminated waters from the dump (see **Figure 1**).

In the sample **no. 17** taken from the Vardar River, before the dump, Cr^{6+} is not detected. In the sample **no. 18** taken from the Vardar River, under the dump, lower concentrations of Cr^{6+} (0.069 mg/l) are registered, which are 7 times higher than the maximum amount allowed.

If we take into account that there is recharging of the Zheden karst aquifer from the Vardar River (**Kekić, 1986**) in the area before and after the dump, it can be concluded that contamination with Cr^{6+} is possible in the future of the groundwater of the Rashche Spring.

6. Conclusions

The obtained results from the performed investigations suggest high contamination of the groundwater and surface waters around the industrial dump Jugohrom with Cr^{6+}, and around the past metallurgy plant Jugohrom in Jegunovce.

The contamination with Cr^{6+} is determined to a higher extent in the unconfined aquifers occurring to a depth of about 23 m, and to a lower extent it is present in the artesian aquifers with sub-artesian level and occurring at a depth to about 100 m.

Contamination with Cr^{6+} is also determined in the water of the Vardar River, under the dump. If it is taken into consideration that there is recharging of the Zheden karst aquifer along the flow of the Vardar River, in the area before and after the dump, and if appropriate measurements are not taken in the future, contamination with Cr^{6+} may occur to the groundwater in the Zheden Massif, and the Rashche Spring, because it is a karst spring discharging from the Zheden Massif.

In order to avoid the contamination with Cr^{6+} of the water discharge from the Rashche Spring, it is necessary to undertake certain preventive measurements with regular monitoring of the surface water and groundwater quality around the dump, and regular treatment of the waters contaminated with Cr^{6+}.

Given the validity of the water from the Rashche Spring, used for water supply of the city of Skopje, a permanent solution to the problem is necessary, or complete removal of the dump, if possible, extraction of the useful mineral raw materials, remediation of the soil and removing the upper contaminated layer, remediation of the groundwater and recultivation of the terrain.

7. References

Arsovski, M. (1997): Tektonika na Makedonija (Tectonics of Macedonia). Univerzitet "Sv. Kiril I Metodi – Skopje" – Fakultet za Rudarstvo i Geologija – Stip.

Dumurdzhanov, N. (1997): Lacustrine Neogene and Proceeding of the Field Meeting held in Yugoslavia in 1995-1996, International Geological correlation project 329, „Neogene of the Paratethys". Belgrad, Special Publication, geoinstitute, no. 21. p. 31-36.

Dumurdzhanov, N. and Serafimovski, T. (2004): Evolution of the Neogene-Pleistocene Basins of Macedonia. Society of America. Digital Maps and Chart Ser. 1, 1-20.

Dumurdzhanov, N., Serafimovski, T. and Burchfiel, B.C. (2005): Cenozoic tectonics of Macedonia and its relation to the South Balkan extensional regime. Geosphere 1, 1:1-22.

Dumurdzhanov, N., Serafimovski, T. and Burchfiel, B.C. (2008): Genesis and lithostratigraphy of the Neogene and Pleistocene basins in Macedonia. First Congress of the geologists of R. of Macedonia. Pg. 29-52. Ohrid.

De Flora, S., Serra D., Camoirano, A. and Zanacchi, P. (1989): Metabolic reduction of chromium, as related to its carcinogenic properties. Biol. Trace Elem. 21:179–187. doi: 10.1007/BF02917250.

Edition, (2018): Drinking Water standards and Advisory Tables, United States Environmental Protection Agency, 8 p.

EC, (1998): Council Directive (98/83/EC) of 3 November 1998 on the quality of water intended for human consumption. Office J Eur Commun, L330.

Fantoni, D., Brozzo, G., Canepa, M. and Cipolli, F. (2002): Natural hexavalent chromium in groundwater interacting with ophiolitic rocks. Environmental Geology, 807-816.

Gebrekidan, M. and Samuel, Z. (2011): Concentration of Heavy Metals in Drinking Water from Urban Areas of the Tigray Region, Northern Ethiopia. CNCS, Mekelle Univesity, 3, 105-121, ISSN: 2220-184X.

Ilijovski, Z., (2013): Hidrogeoloska karta na R. Makedonija vo merka 1:300 000 (*Hydrological map of R. of Macedonia, Scale 1:300 000*).

Ilijovski, Z., Mihailovski, S., Ivica, A., Makeshoska, M. (2019): Expertise for editing the protection zones limits of Rashche spring and determining protection measurements. Civil Engineering Institute „Macedonia" – Skopje.

Ilijovski, Z., Mihailovski, S., Ivica, A., Makeshoska, M., Lefkov, D. (2020): Study for redefining the hydrogeological condition of the groundwater in the area between Jegunovce dump and Vardar River in terms of Rashche Spring protection. Civil Engineering Institute "Macedonia", Skopje.

Jančevski, J., Galabov, K., Temkova, V. (1982): Tolkuva**č** za Osnovna geolska karta na RM, za list Skopje, vo merka 1:100 000. (*Interpreter of Basic geological map of RM, Scale 1: 100 000, sheet Skopje*). Geoloski Zavod Skopje.

Jančevski, J., Popvasilev, V. (1982): Osnovna geoloska karta na Republika Makedonija, vo merka 1:100 000, za list

Skopje. (*Basic geological map of RM, Scale 1:100 000, sheet Skopje*). Geološki Zavod Skopje.

Kekić, A. (1986): Geologija i Hidrogeologija na Poloskata kotlina i poteklo na vodata na izvorot Rasce *(Geology and Hydrogeology of the Polog basin and origin of the water from Rashche spring*). Geoloski zavod Skopje.

Koleli, N. and Demir, A. (2016): Environmental Materials and Waste. Academic Press; London, UK. https://scholar.google.com/scholar_lookup?title=Environmental+Materials+and+Waste&author=N.+Koleli&author=A.+Demir&publication_year=2016&

Lyon, (2012): IARC CHROMIUM (VI) COMPOUNDS. *Arsenic, Metals, Fibres and Dusts.* International Agency for Research on Cancer, France. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. https://scholar.google.com/scholar_lookup?title=Arsenic,+Metals,+Fibres+and+Dusts&publication_year=2012&

Official Gazette of Republic of Macedonia, (1984): Rulebook for the quality and health safety of drinking water, Nr. 5/1984.

Pellerin, C. and Booker, S. M. *(*2000): Reflections on hexavalent chromium: Health hazards of an industrial heavyweight. Environ. Enviromental Health Perspect. 2000;108:A402–A407. doi: 10.1289/ehp.108-a402. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2556938/

Petkovski, P., Popovski, S. (1985): Tolkuva**č** za Osnovna geoloska karta na RM, za list Ka**č**anik, vo merka 1:100 000 (*Interpreter of Basic geological map of RM, S*cale *1:100 000, sheet Kacanik*). Geološki zavod Skopje.

Radovanović, M., Pavlović, D., Chukić, Z., Jovashević, D., Keckarević, D. (1989): Study of rehabilitation of Jugohrom plant and chrome sludge dump and chrome content in the groundwaters and waters of Vardar River. Institute for Water Resources Management Jaroslav Cherni - Belgrade.

Soro, A., Hiba, B., Dzhurich, D., Jevtich, G., Popovich, L., Svrkota, D. (2001): Main Design for treatment of the waste waters from the industrial dump HPP Jugohrom and their transportation to the waste water treatment plant, Book 1. Technological-Hydro construction section. Jaroslav Cherni Institute for Water Resources Management – Belgrade, 2001.

Stepek, J., R.G., C.E.G., C.H.G. (2020): DRAFT GROUNDWATER INFORMATION SHEET Chromium VI. In: SWRCB-Division of Clean Water Programs Groundwater Special Studies Unit.

Tumalo, M., Ancoca, V., De Paola, D., Losacco, D., Campanale, C., Massarelli, C. and Felice, U. V. (2020): Chromium pollution in European Water, Sources, Health Risk, and Remediation Strategies: An Overview. International Journal of Environmental Research and public Health. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7432837/

Third edition, (2008): Guidelines for drinking water quality. World Health Organization, Geneva, 334 p.

Vasilatos, Ch., Megremi, I. and Economou-Eliopoulos, M. (2010): Geochemical characteristics of natural waters contaminated by hexavalent chromium, in Eastern Sterea Hellas, Greece. Scientific Annal, 347-353.

Vasilatos, Ch., Megremi, I., Economou-Eliopolus, M. and Mitsis, I. (2008): Hexavalent chromium and other toxic elements in natural waters in Thiva-Tanagra-Malalasa Basin, Greece. Hellenic Journal of Geosciences, 43, 57-66.

Annual reports for the work of PE Water Supply and Sewage, Skopje, 2007-2015 (in RN Macedonia).

SAŽETAK

Zagađenje s Cr^{+6} podzemnih i površinskih voda s industrijskoga odlagališta Jugohrom – Jegunovce, Republika Sjeverna Makedonija

Kako bi se istražilo zagađenje šesterovalentnim kromom (Cr^{6+}) podzemnih i površinskih voda oko industrijskoga odlagališta otpada Jugohroma – Jegunovce provedena su hidrogeološka istraživanja tijekom studenoga 2019. godine. Uzeto je 16 uzoraka podzemnih i 3 uzorka površinskih voda. Koncentracije Cr^{6+} u većemu dijelu analiziranih uzoraka podzemnih i površinskih voda nadilaze najveće dopuštene koncentracije od 0,01 mg/l prema makedonskome i europskim standardima o pitkoj voda. Najveće onečišćenje Cr^{6+} kreće se u rasponu 0,052 – 132,98 mg/l, a opaženo je u blizini plitkih podzemnih ili slobodnih vodonosnika. U arteškim vodonosnicima sa subarteškom razinom vode u nekim uzorcima opaženo je onečišćenje Cr^{6+} 0,017 – 0,041 mg/l. Načinjena su dva ispitivanja na površinskim vodama rijeke Vardar, ispred i iza odlagališta otpada. Koncentracija Cr^{6+} (0,069) povećana sedam puta pronađena je uz odlagalište otpada. U preljevnoj vodi iz drenaže utvrđen je sadržaj Cr^{6+} od 725 mg/l. Zagađenje podzemnih i površinskih voda s Cr^{6+} antropogeno je, a rezultat je rada Metalurškoga postrojenja Jugohroma u razdoblju od 1955. do 1994. godine.

Ključne riječi:
šesterovalentni krom Cr^{6+}, podzemne vode, zagađenje, Zeden, izvor Rašče

Author’s contribution:

Stojan Mihailovski (master student, hydrogeology) performed field sampling of groundwaters and surface waters and graphical processing of the hydrochemical data. **Vojo Mircovski** (Dr., Full Professor, geology) participated in the analyses and interpretation of hydrochemical data for groundwater. **Zlatko Ilijovski** (Dr., Associate Professor, hydrogeology) performed interpretation of the hydrogeological and geological characteristics of the terrain.