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# HEAVY METALS IN THE WATER OF HYDRO-ACCUMULATION MAVROVICA – EASTERN MACEDONIA

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*Abstract*

*In this paper the results and conclusions from the researches of the pollution of the water with heavy metals in the drain-basin of Mavrovica hydro accumulation are given. With our analysis, there is an effort made to see the real conditions in the examinated area, and to determine the position of presence of heavy metals in the water of the above mentioned accumulation. The samples of water were taken from several places from the hydro-accumulation, and the same are representative and suitable for the condition of the area. The analysis of the taken samples was made in the frames of one sequence of analysis of the instrument Atomic emissive spectrometry, with inductive harnessing plasma (AES-ICP). From the last examinations of contaminated areas, as our area of interest, we can notice that the following group of elements should be kept track of: Mn, Fe, Al, Pb, Zn, As, Cd, Cu, Ni, Co, Ag, Cr, Ti with the possibility of several elements that will show higher concentrations of MAA (maximum allowed amounts).*
*After the analysis and interpretation of the data, the assumptions were confirmed for increased values of the following metals: Al, Mn, Fe, Zn, As, Cd, Cu.*
*Increased concentrations of some of the metals very often were several times above the maximum allowed concentrations.*

*Key words: heavy metals, pollution, AES-ICP, hudro-accumulation, Mavrovica, increased concentrations, water, maximum allowed concentrations.*

## Introduction

The pollution of the living environment in the past several decades is a subject on which is given minimal attention, but in the last few years this subject has priority meaning. From big importance is the problem for the presence of the heavy and toxic metals in the water. It is necessary to appoint the presence of the metals – contaminates in the drinking water. Actualizing this question it must to be appointed that water supplying with drinking water in SvetiNikole in the last period is done exceptionally trough hydro-accumulation Mavrovica.
Because of the suspicious quality of the water from the above mentioned accumulation, in 2003 an act was brought out for forbidding for usage of the water from this accumulation as a drinking water. Having in mind this fact, the necessity of one more studious analysis of the quality of the water from the accumulation has showed.
In the nearby surrounding of the above mentioned area there are numerous agricultural surfaces, that are used for manufacturing different agricultural cultures. Past investigations from geological-geochemical and ecological aspect are showing the potential possibilities for natural pollution in the examinated area. Even more significant reason for accomplishing this theme are more and more rigorous legal measurements for the quality of the living environment in which the people from this region live, stay and work.
In the studying of the chemical and geochemical characteristics of the water from hydro-accumulation Mavrovica and it's near surrounding a small number of explorers have taken part.

The data base that are concerning the problems that are the subject of this examinations can be appointed in the thesis of Spasovski and others [8,9,10], Rakicevic and others [7], Guzelkovski[3], Karajovanovic and others [5-6], Dumurdjanov and others [4].
The space that was a subject of the research embraces the area of hydro-accumulation Mavrovica which is placed about 4 km North-east from SvetiNikole. (Picture 1)


*Picture 1. Map of Republic of Macedonia with specified location of the researched area.*

## Material and methods

In the frames of the foreseen investigations, there are basic field activities done, that are consisted of preliminary following of the field with topographic determinations of the points of appropriation, and determination of the profile lines in which the water samples will be taken. In the frames of this phase the field that embraces the space of the mentioned accumulation was cultivated.
The starting phase of the determination was consisted of taking samples of water from the above mentioned points. Taking the water samples was from the middle of the accumulation in appropriate clean plastic dish (plastic bottle of 1 l). It is necessary to mention that during taking the samples from the water, their filtration is done at the same time, trough filtration trough filter paper with width of the holes of 45 μм.
Before closing the dishes acidifying is done with 0.4 ml from 50% nitric acid ($HNO_3$). This measure of caution is done to prevent deposition of the metals on the walls and in the bottom of the dish. Taking the samples was with exact determination of the points of determination with the help of topographic map in proportion 1: 20 000. The laboratory examinations are consisted of analysis of taken samples with the method AES-ICP and interpretation of the gained results.

*Picture 2. Look of the hydro-accumulation Mavrovica*

**Results and discussion**

In the frames of the foreseen examinations the samples from the water from the periphery and the middle parts of the accumulation were taken.
The results gained for the contents of the heavy metals in the water from hydro-accumulation Mavrovica are given in Table 1.
To get more complete impression for the concentration of the analyzed elements in the water samples taken from hydro-accumulation Mavrovica, in the further examinations will be thoroughly presented and commented the data gained with the examinations.
In the same table the standards for the content of the analyzed elements in the water are given, with aim to compare the gained results with the standards.
On the base of the data shown in Table 1, certain notes can be given for the presence of the certain heavy metals in the water from her influents, and also an opinion for the reasons for the causes that contribute for the increased contents of the certain metals.
*Calcium* – in the samples taken from the hydro-accumulation Mavrovica is shown in contents lower than maximum allowed concentrations. Highest values for calcium are consisted in the sample Mv-3 (77.16), and lowest values we have in the sample Mv-1(64.10)
*Magnesium* – unlike calcium in all the samples is shown in amounts lower than maximum allowed concentrations. Highest values are consisted in the sample Mv-3 (18.33 mg/l).
The data for the iron (Table 1) are showing its small presence in the biggest number of the analyzed samples and values lower compared to maximum allowed. In the samples Mv-2 and Mv-3 the iron is shown in higher concentrations (0.074 and 0.056 mg/l) but anyway they are lower than maximum allowed.
*Aluminum* presents biggest contaminate of the whole examinated area. In the samples of water taken from the hydro-accumulation during the examination, the values that are gained are higher than maximum allowed concentrations.
The values gained for the aluminum in the samples from the water from hydro-accumulation Mavrovica are moving in the limits from 0.51 mg/i (Mv-1) to 0.72 mg/l (Mv-3).
Former examinations made for the content of aluminum in the sediments, has shown values higher 100 times, which shows that the level of the aluminum presence in the researched area is high, but because of its geochemical characteristics and pH of the water, the same is sediment.

*Table 1: Concentrations of heavy metals in the samples of water from hydro-accumulation Mavrovica and standards in (mg/l)*

| Elements | Oznakanaprobite | | | | | Srednavrednost |
|---|---|---|---|---|---|---|
| | Mv-1 | Mv-2 | Mv-3 | Mv-4 | Mv-5 | Sr |
| As | 0.078 | 0.005 | 0.005 | 0.008 | 0.005 | 0.028 |
| Stand | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Se | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 | 0.0057 |
| Stand | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Ag | 0.001 | 0.000 | 0.002 | 0.001 | 0.002 | 0.0025 |
| Stand | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 |
| Al | 0. 51 | 0.55 | 0.72 | 0.57 | 0.52 | 0. 574 |
| Stand | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Ca | 64.10 | 71.96 | 77.16 | 66.25 | 66.39 | 69.865 |
| Stand | 200 | 200 | 200 | 200 | 200 | 200 |
| Ni | 0.005 | 0.005 | 0.005 | 0.007 | 0.005 | 0.007 |
| Stand | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Mn | 0.001 | 0.001 | 0.061 | 0.06 | 0.001 | 0.002 |
| Stand | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Fe | 0.0069 | 0.074 | 0.056 | 0.010 | 0.007 | 0.0429 |
| Stand | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Cr | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Stand | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Mg | 14.67 | 17.00 | 18.38 | 15.38 | 15.18 | 17.886 |
| Stand | 150 | 150 | 150 | 150 | 150 | 150 |
| Zn | 0.004 | 0.005 | 0.006 | 0.003 | 0.003 | 0.006 |
| Stand | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Cu | 0.002 | 0.001 | 0.005 | 0.002 | 0.008 | 0.0041 |
| Stand | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Pb | 0.005 | 0.005 | 0.005 | 0.005 | 0.0019 | 0.004 |
| Stand | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Cd | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Stand | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| Co | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Stand | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| pH | 6.93 | 6.91 | 6.92 | 6.91 | 6.93 | |

*The Zinc* does not presents contaminate of the researched area. The values gained for the zinc (Table 1) are confirming its presence in the researched area, but they are significant lower compared to the maximum allowed.

*Manganese* is seen in all of the analyzed samples from which in 3 (Mk-1, Mk-2 and Mk-3) with lower values, and in 2 samples (Mk-3 and Mk-4) with values higher than maximum allowed. The gained values for the manganese during the research are confirming its presence in the area.

*Nickel, cobalt and cadmium* are seen in all of the examinated samples, but with values lower than maximum allowed concentrations.

*Cuprum, plumbum and chrome* are seen in all of the examinated samples, and are in concentrations lower than maximum allowed concentrations and don't represent contaminates of the studied area.

## Conclusion

According the results that are gained from the chemical researches, for the contents of the heavy metals in the water from hydro-accumulation Mavrovica, it can be concluded that a certain group of elements (Al, Mn, Fe) in most of the examinated samples are gained values higher than maximum allowed concentrations, other group of elements (Ni, Co, Cd, Zn) are seen in lover concentrations but still close to the standard values, and third group of elements (Cu, Pb, Cr) are showing much lower values than maximum allowed concentrations. Surveys indicate that there is a law of the distribution of element contaminants, or their continuous monitoring and gradually increasing in some samples. This way of matching element contaminants indicates presence of the analyzed elements in the water of the hydro-accumulation Mavrovica.
For the concentration of metals in the water influence has the geological composition of the studied area, geochemical characteristics of the elements contaminants, as well as pH and Eh factors.
The presented findings and conclusions are based on a relatively small number of examinations (total of 5 samples of water) but anyway reflect the presence of a certain group of elements contaminants. The obtained values for examinated elements initiate a number of problems (examination of the watershed area of the hydro-accumulation Mavrovica, monitoring of the water in different time periods, examining the mineralogical and chemical composition of the environment through which the running water is passing) in order to understand the source of contamination and the impact of the elements contaminants on the living environment.

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