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Faculty of Natural and Technical Sciences	**Факултет за природни и технички науки**
P. O. Box 96	**пошт. фах 96**
MK-2000 Štip, Republic of Macedonia	**МК-2000 Штип, Република Македонија**
Tel. ++ 389 032 550 575	**Тел. 032 550 575**

E-mail: todor.serafimovski@ugd.edu.mk

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Original scientific paper

HEAVY METALS IN THE WATER FROM THE DRAIN-BASIN OF THE MAVROVICA HYDRO-ACUMULATION – EASTERN MACEDONIA

Orce Spasovski, Trajče Mitev

Faculty of Natural and Technical Sciences, "Goce Delčev" University,
Goce Delčev 89, MK-2000, Štip, Republic of Macedonia
orce.spasovski@ugd.edu.mk // trajce.mitev@ugd.edu.mk

A b s t r a c t: 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 basin. The samples of water were taken from river Orelska and the smaller rivers (streams) near river Orelska. The analyses of the taken samples were 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. The whole drainage system that gravitates trough river Orelska is contaminated. Increased concentrations of some of the metals were very often, several times above the maximum allowed concentrations.

Key words: heavy metals; pollutions; AES-ICP; water; river Orelska; river Makreska, river Kiselička, drainage area

INTRODUCTION

The pollution of the living environment in the past several decades is subject of which was given very little attention, but in the last several years this is very delicate subject with high priority. Very important is the problem of heavy metal and toxic metals presence – contaminates in the drinking water. Actualizing this question, we must say that the supply with drinking water, of the local population in the past period is strictly from the hydro-accumulation Mavrovica. Because of the suspicious quality of the water from the above mentioned accumulation during 2003 there was a decision made, for forbidding the further usage of the water of this accumulation for drinking water. Having this fact in mind there is a need for one more studious analysis of the water in this drainage-area.

There are more confluents of river Orelska that are used by the local inhabitants f or different needs. In the near by environment of the above mentioned area, there are large number of agricultural surfaces that are used for manufacturing different agricultural products. The last geological, geochemical and ecological researches showed the potential possibilities of natural pollution in the examined area. Even more significant reason for getting across this thesis is more and more strict legal standards for the quality of the living environment in which people lives, and work in this region.

In the research of the chemical and geochemical characteristics of the flowing water from the drainage area of the Mavrovica hydro-accumulation, and her near surrounding, in this period, were very little examinated. The data from this researches can be found in the papers of Ракичевиђ at al. (1968), Карајовановиђ at al. (1975а and 1975б), Думурџанов at al. (1976), Ѓузелковски (1997). Spasovski at al. (2007, 2009, 2010).

The area that was under research is covering river Kiselička, river Makreska and river Orelska until it's infusion in the Mavrovica accumulation (Fig. 1).

Fig. 1. Map of Republic of Macedonia with specified condition of the researched area

MATERIAL AND METHODS

In the frames of the researches there were preliminary field activities made, that were consisted from preliminary monitoring of the area, in order to gain preliminary impressions of the field.

Starting the field experiments there are the points of research defined, and in the same time the profile lines, which are defining basic field of research were defined. In the frames of foreseen activities, there are basic field researches made, that are consisted of preliminary tracking the field trough topographic determinations of the points of testing, and determination of the profile lines, from which the water samples will be taken. In the frames of this phase the field that embraces the flow of river Orelska and surrounding streams, starting from river Kiselička trough Blagin dol, to the inculcation of river Makreska in river Orelska, continuing to the inculcation to the mentioned hydro-accumulation were cultivated.

Starting phase of the experiment was taking samples from water from the named points of examination. Taking the samples from water is consisted from taking samples of water from the middle of the river flow, in clean plastic dish (plastic bottle from 1 L).

It is necessary to say that during assumption of the samples from the water, in the same time the filtration is done, trough paper filter with dimensions of the caliber of 45 μm. Before closing down the dishes, acidifying with 0.4 ml from 50% nitrogen acid (HNO_3) is done. This measure of caution is done in order to prevent sedimentation of the metals on the walls and the bottom of the dishes. Taking the samples was followed with certain determination of the points of experiment with help of topographic map in proportion 1 : 25 000. Laboratory examinations are consisted from analysis of taken samples with the method AES-ICP and interpretation of the gained results.

RESULTS AND DISCUSSION

In the frames of the foreseen examinations, samples from the water were taken from the middle of the river flow where the water shows calm flow. Every test is marked with unique number, and the places of the taken samples in the field are shown on the topographic map (Fig. 2).

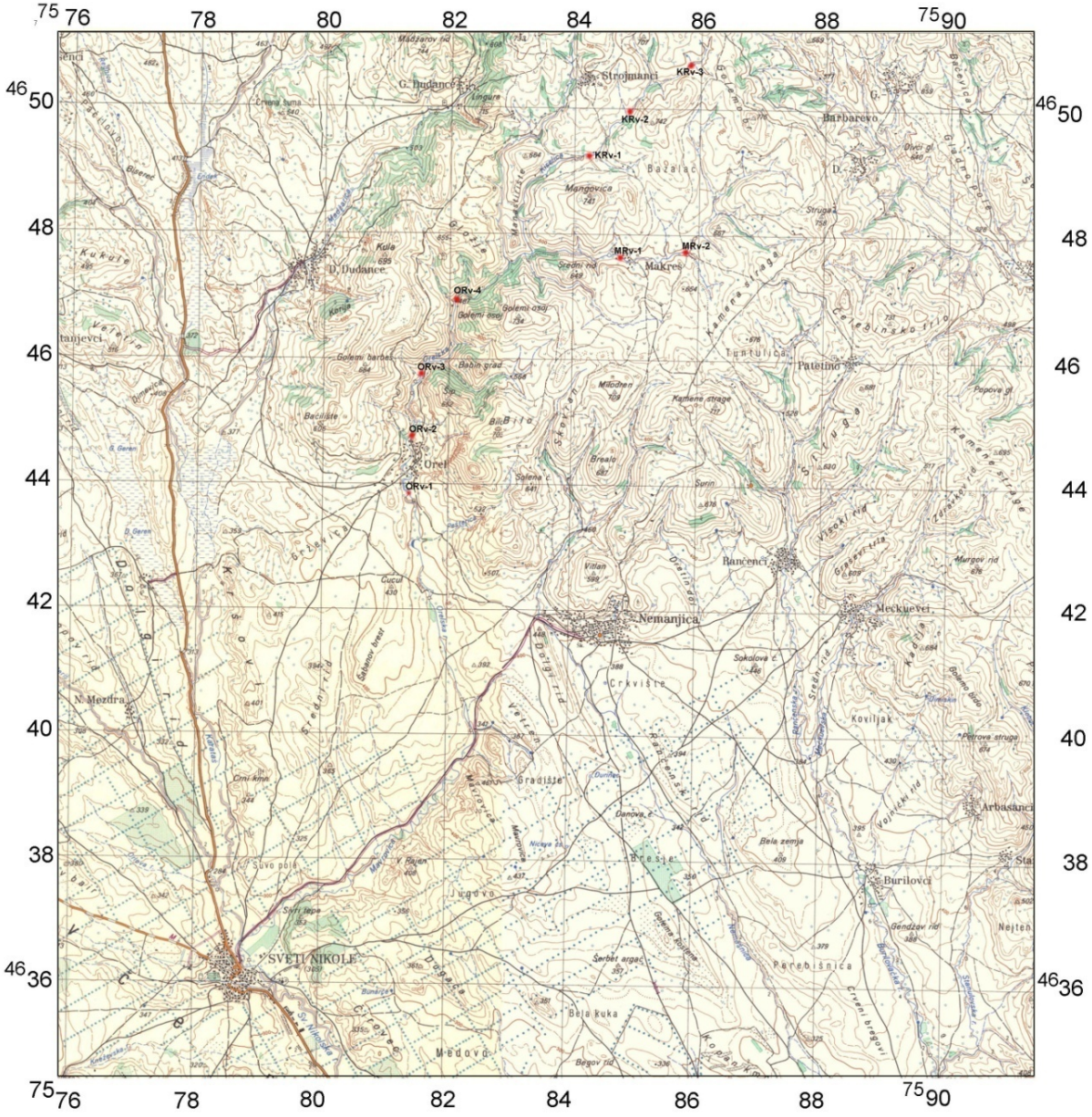

Fig. 2. Topographic map with pointed places of taken samples of water.

The results that are gained for the contents of the heavy metals in the water from the drainage basin of hydro-accumulation Mavrovica are given in Table 1.

To receive more complete impressions for the concentration of the analyzed elements, in the samples of water, taken from the drain area of Mavrovica hydro-accumulation, in the further examinations will be exhaustively presented and commented the results given in Table 1.

In the same table there are also given the standards for the contents of the analyzed elements in the moving water, in order to compare gained results with the standards.

In the basis on the data, given in Table 1, certain notes can be given, about the presence of certain heavy metals in the water from her confluents, and also the opinion for the reasons that redound to increased contents of certain metals.

Calcium in the tests taken from river Orelska and Makreska is showing in amounts, smaller than maximum allowed concentrations. In the tests taken from river Kiselička calcium is showed in values higher than maximum allowed concentrations. Highest values for magnesium are seen in the test KR-3 (279.60).

Table 1

Content of heavy metals in the flowing water from the drainage basin of Mavrovica hydro-accumulation.

	ORv-1	ORv-2	ORv-3	ORv-4	MRv-1	MRv-2	KRv-1	KRv-2	KRv-3
As	0.008	0.005	0.111	0.001	0.004	0.035	0.0001	0.0001	0.0001
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Se	0.008	<0.005	0.035	0.004	0.005	0.004	0.0001	0.0003	0.0001
Stand	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ag	0.012	<0.001	0.001	0.004	0.005	0.004	0.0001	0.0003	0.0001
Stand	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Al	0.003	0.002	0.012	0.238	4.67	5.21	69.15	71.12	72.89
Stand	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ca	78.545	60.026	74.492	68.07	96.19	90.15	279.20	266.14	279.60
Stand	200	200	200	200	200	200	200	200	200
Ni	0.003	0.032	0.021	0.004	0.0054	0.0050	0.0050	0.049	0.052
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Mn	0.013	0.010	0.016	0.012	0.0049	0.005	4.41	4.93	5.47
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Fe	0.089	0.020	0.081	0.062	0.029	0.032	5.45	5.76	5.95
Stand	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Cr	0.001	<0.001	<0.001	0.001	0.004	0.004	0.001	0.001	0.001
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Mg	18.765	23.449	20.266	15.42	16.23	17.46	52.14	47.12	52.09
Stand	150	150	150	150	150	150	150	150	150
Na	20.700	21.526	19.198	22.46	29.06	29.20	66.79	63.45	66.79
Zn	0.009	0.011	0.081	0.579	0.012	0.010	0.61	0.55	0.71
Stand	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cu	0.006	0.008	0.009	0.008	0.011	0.010	0.022	0.023	0.028
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Pb	0.001	0.001	0.010	0.017	0.007	0.006	0.002	0.001	0.002
Stand	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cd	0.001	<0.001	<0.001	0.001	0.0017	0.0018	0.0032	0.0033	0.0048
Stand	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Co	<0.001	0.001	0.014	0.026	0.017	0.019	0.142	0.145	0.150
Stand	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Na	20,700	21,526	19.198	22.46	28.12	29.06	55.14	58.15	66.79
K	4.041	3.503	5.588	5.852	6.976	6.986	9.451	9.392	9.426
pH	5.98	6.81	6.88	5.93	–	–	–	–	–

Symbols of taken samples: ORv – sample of water taken from river Orelska; MRv – sample of water taken from river Makreska; KRv – sample of water taken from river Kiselička

Magnesium, not like calcium, in all the tests is shown in concentrations lower than maximum allowed concentrations. What is interesting for this element is gradually increasing its values, going towards headwater of the studied rivers, and especially river Kiselička where are the highest values of 52.09 mg/l (sample KRv-3).

The values gained for alkaline metals Na and K are showing significant variation in the analyzed samples. The values that are gained for Na are moving in the frames from 19.198 mg/l in the sample ORv-3 to maximum of 66.79 mg/l in the sample KRv-3. Potassium is shown in concentrations significantly smaller compared to Na, and the

same are moving in the frames from 5.03 in the sample ORv-2 to maximum 9.451 mg/l in the sample KRv-1.

The data for ferum (Table 1) are showing its small presence in the largest number of analyzed samples. The exception makes only the samples of water from river Kiselička, where the ferum is noted with values larger than maximum allowed concentrations and are moving in the frames from 5.45 mg/l (sample KRv-1) to 5.95 mg/l (sample KRv-3). Down the river Kiselička flow, a red deposit can be noticed, because of the presence of the oxides if ferum, but also the water is showing acetic taste.

Aluminum presents the biggest infector of the whole studied area. In the water samples taken from river Orelska, the values that are gained during the examination are lower than maximum allowed concentrations. The values gained for the aluminum in the samples of water in river Makreska and river Kiselička are showing its significant presence in this two rivers. Namely, the values for aluminum in the samples of water from river Makreska, are more than 10 times higher than maximum allowed concentrations. The results that are gained for the aluminum in the analyzed water samples from river Kiselička are showing very large contamination of this space with aluminum, indeed the values that are higher over 146 times compared to standards.

Significant infector of the studied area is also the zinc. The values gained for zinc in river Orelska (0.579 mg/l) and in the samples of water from river Kiselička (0.55 to 0.71 mg/l), are confirming very clearly its presence in the studied area. These values are showing that the concentrations of zinc are 7 times higher compared to the standards.

Manganese, like the zinc is significant infector of the researched area. The values that are gained for manganese in the river Kiselička are moving in the frames from 4.41 to 5.47 mg/l are around 10 times higher compared to the standards, and by that, it is confirmed its large presence in the examinated area.

Nickel, cobalt and cadmium are noted in every examinated samples, but the values that are gained in the largest number of the samples are lower than maximum allowed concentrations. In the samples of water taken from river Kiselička, of the above mentioned elements, the values that are gained that are higher, but also very close to the standard values.

Cuprum, plumbum and chrome in all tested samples are shown in concentrations that are lower than MDK and are not presenting contaminates in the researched area.

CONCLUSION

According the results that are gained, from the accomplished chemical researches for the content of heavy metals, in the flowing water from drainage basin of hydro-accumulation Mavrovica, it can be concluded that certain group of elements (Al, Mn, Zn, Fe), in biggest part from researched samples, are showing significant enlargement compared to MDK. Other group of elements (Ni, Co, Cd) is showed in concentrations very similar to the standard values, and the third group is elements (Cu, Pb, Cr) that are showing very low values according to MDK.

The researches are showing that there is legislative in the allocation of the elements that are infectors, in fact their continuous tracing and gradually enlargement of their values starting from river Orelska to Kiselička. This kind of appearance of the elements-contaminants, clearly can locate the natural source of contamination, the area around the source of river Kiselička.

For the metal concentrations in the flowing water, geological composition of the researched area has influence, geochemical characteristics of the elements-contaminates, as well as pH and Eh factors.

This conclusions and notes are based on relatively small number of researches (total 9 samples of water), but any way they are giving clear picture for presence of certain group of elements-contaminants. The values that are gained for the examinated elements, are initializing larger amount of problems (research of inculcation of river Orelska in hydro-accumulation Mavrovica, awareness for the composition of water in hydro-accumulation, monitoring of the water in different time periods, examinations of mineralogical and chemical composition of the environment trough where the flowing water are passing) with aim to see the source of contamination and the influence of the elements that are contaminants of the living environment.

REFERENCES

Alloway, B. J., and Ayres, D. S., 1963: *Chemical Principles of Environmental Pollution*, Blackwell Scientific, Publications, London.

Appelo C. A. J., Postma, D., 2005: *Geochemistry, Groundwater and pollution. 2nd Edition*. A. A. Balkema, Rotterdam/ Brookfield. pp. 649.

Ѓузелковски, Д., 1997: *Подземните води (издан) за решавање на водоснабдувањето на Република Македонија и нивна заштита*, Институт Геохидропроект, Скопје.

Думурџанов, Н., Христов, С., Павловски, Б., Иванова, В., 1976: *Толкувач за основната геолошка карта на Република Македонија за листот Штип*, ОГК СФРЈ 1 : 100 000, Геолошки завод Скопје.

Карајовановиќ, М., Хаџи-Митрова, С., Аранѓеловиќ, Р., 1975а: *Основна геолошка карта на Република Македонија за листот Титов Велес*, ОГК СФРЈ 1 : 100 000, Геолошки завод Скопје.

Карајовановиќ, М., Хаџи-Митрова, **С.,** 1975б: *Толкувач за листот Титов Велес*, ОГК СФРЈ 1 : 100 000, Геолошки завод Скопје.

Ракичевиќ, Т., Думурџанов, Н., Петковски, П., 1968: *Основна геолошка карта на Република Македонија за листот Штип*, ОГК СФРЈ 1 : 100 000, Геолошки завод Скопје.

Spasovski, O., Doneva, B., 2007: *Heavy metals in the water of the River Zletovska and the Vicinty*. 2nd Balkan mining congress, Belgrade.

Spasovski, O., Dambov, R., 2009: *Heavy Metals in the Water of the River Kalništanska and the Vicinty*. 3rd Balkan Mining Congress, Izmir-Turkey, pp. 667–671.

Spasovski. O., Ristova, J., Mitev, T., 2010: *Heavy metals in sediments of Artifical Hydro Accumulation Mavrovica and Orelska Reka, Eastern Macedonia*. 15 th Congress of Geologists Serbia, With International participation, Belgrade, pp. 657–661.

Р е з и м е

ТЕШКИ МЕТАЛИ ВО ВОДАТА ОД СЛИВНОТО ПОДРАЧЈЕ НА ХИДРОАКУМУЛАЦИЈАТА МАВРОВИЦА Ђ ИСТОЧНА МАКЕДОНИЈА

Орце Спасовски, Трајче Митев

Факултет за природни и технички науки,Универзитет вГоце Делчевв, Гоце Делчев 89, МК-2000, Штип, Република Македонија
orce.spasovski@ugd.edu.mk // trajce.mitev@ugd.edu.mk

Клучни зборови: тешки метали; загадување; AES-ICP; вода; Орелска Река; Макрешка Река; Киселичка Река; сливно подрачје.

Во овој труд се дадени резултатите и заклучоците од истражувањата на загадувањето со тешки метали во водата од сливното подрачје на хидроакумулацијата Мавровица. Со нашите испитувања, направен е обид да се согледаат реалните состојби во испитуваниот простор и да се утврди состојбата за присутноста на тешките метали во водите на споменатиот простор. Примероци на вода беа земени од Орелска река и помалите реки од нејзината непосредна околина. Анализата на примероците беше спроведена во рамките на една серија на анализи на инструментот Атомска емисиона спектрометрија со индуктивно спрегната плазма (AES-ICP). Од досегашните искуства на контаминирање на подрачја какво што е подрачјето од интерес, може слободно да се констатира дека треба да се следи следната група на елементи: Mn, Fe, Al, Pb, Zn, As, Cd, Cu, Ni, Co, Ag, Cr, Ti со можност и некои елементи кои ќе покажат поголеми концентрации од МКД (Максимално дозволени количества).

По анализата и интерпретацијата на податоците беа потврдени претпоставките за зголемени вредности на следните метали: Al, Mn, Fe, Zn, As, Cd, Cu. Контаминиран е целосниот дренажен систем кој гравитира кон Орелска река.

Зголемените концентрации на некои од металите многу често беа за неколку пати поголеми од максимално дозволените концентрации.