# XI YUCORR

## INTERNATIONAL CONFERENCE

# PROCEEDINGS

## COOPERATION OF RESEARCHES OF DIFFERENT BRANCHES IN THE FIELDS OF CORROSION, MATERIALS PROTECTION AND ENVIRONMENTAL PROTECTION

# KNJIGA RADOVA

## SARADNJA ISTRAŽIVAČA RAZLIČITIH STRUKA NA PODRUČJU KOROZIJE, ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE

*Pod pokroviteljstvom*

**MINISTARSTVA ZA NAUKU I TEHNOLOŠKI RAZVOJ REPUBLIKE SRBIJE**

*Under auspices of*

**MINISTRY OF SCIENCE AND TECHNOLOGICAL DEVELOPMENT REPUBLIC OF SERBIA**

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**IZDAVAČ**
SAVEZ INŽENJERA SRBIJE ZA ZAŠTITU
MATERIJALA (SITZAMS), 11000 BEOGRAD,
KNEZA MILOŠA 7a/II, tel/fax: +381 11 3230 028
E-mail: sitzams@eunet.rs
www.sitzam.org.rs

**ZA IZDAVAČA**
*Prof. dr MIOMIR PAVLOVIĆ, predsednik SITZAMS*

**ORGANIZACIONI ODBOR**
*Prof. dr Časlav Lačnjevac, prof. dr Miomir Pavlović, dr Vladimir Panić, dr Nebojša Nikolić, dr Miodrag Stojanović, Zagorka Bešić, dipl inž., Miomirka Anđić, dipl. inž.,*

**UREDNICI**
*Prof. dr Miomir Pavlović*
*Prof. dr Časlav Lačnjevac*

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*Dušan Karadžić*

**ŠTAMPA**
*„FOTO FUTURA"*
*E-mail: karadzici@nadlanu.com*

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**REKLAME**

# THE FUTURE-ORIENTED SOLUTION DESIGNED FOR THE EVER INCREASING REQUIREMENTS IN WASTEWATER TREATMENT AND FOR MAXIMUM EFFLUENT QUALITIES

Trajce Mitev, Orce Spasovski

*Faculty of Natural and Technical Sciences,*
*Goce Delcev University, Stip, R. Macedonia*

## ABSTRACT

*This paper is about a future-oriented solution for membrane wastewater treatment presenting a 1000 inhabitants design concept and its investment costs. The wastewater of connected residential estates, or directly from a complete hotel for example, flows into a buffer tank. Then the flow is passed through a preliminary screen (HUBER fine screens) to remove coarse material before it enters the bioreactor of the HUBER BioMem® Complete Plant where the pollutants contained are decomposed biologically. A submersible pump delivers the wastewater then into the filtration chamber where the activated sludge and clarified water are separated. Due to the low separation size of 38 nm not only all solids but also all bacteria and virtually all germs are retained and remain in the sludge that has to be removed regularly. The effluent can directly be reused for irrigation or infiltration (groundwater recharge) or as service water, or may be discharged into a receiving water course.*

## Introduction

In many countries wastewater disposal and treatment are still underdeveloped. Wastewater is often discharged into nearby rivers or the sea, or infiltrated without prior treatment. The negative effects are pollution of potable water reservoirs, eutrophication of waters and pollution of beaches with washed ashore material. An additional problem in arid and semi-arid areas is water shortage. For improved environmental protection and the need to close the water cycle, special technologies are becoming increasingly important, such as the HUBER BioMem® that is based on the most advanced technology presently available for treatment of municipal and industrial wastewater.

The HUBER BioMem® System (Picture 1) is a complete clarification plant for decentralized applications, consisting of mechanical preliminary treatment, bio-stage and a filtration chamber with HUBER VRM® (Vacuum Rotation Membrane) Unit. The principle of membrane filtration is based upon the separation of solids suspended in a watery solution by means of a pressure difference. While the water permeates through the membrane, the solids, bacteria and even most viruses are retained on the concentrate side on the membrane surface where they are removed by relative movement. The pressure differential necessary to pass the liquid through the membrane depends on the membrane pore size and membrane quality. The submerged HUBER VRM® ultrafiltration membranes retain all solids, bacteria and germs bigger than approx. 38 nm separation size and guarantee thus a maximum effluent quality. Compliance with latest legal effluent standards and reuse of the water as service water is possible without the need for additional treatment stages. The modular design allows for realisation of various system sizes for municipal applications.[1]

## Choosing VMR unit

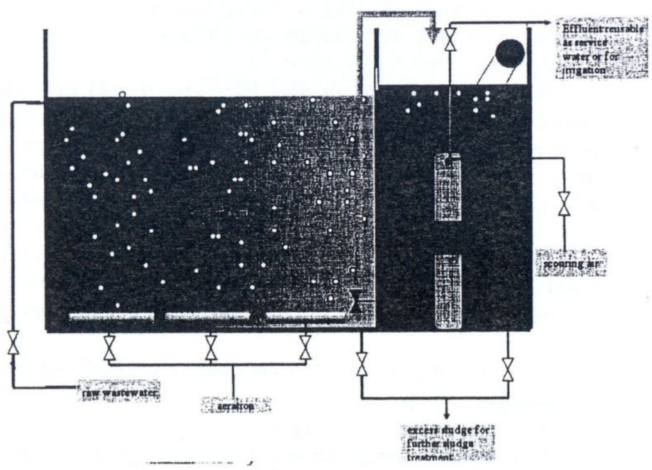
This VMR unit is to provide for 1000 inhabitants. The current Macedonian maximum allowed $BOD_5$ is below 20 mg/l. The maximum amount of mixed liquor suspended solids should not exceed 30 mg/l.

*Table 1: Input parameter*

| Number of the inhabitants (inh) | Waste water quantity | $BOD_5$ |
|---|---|---|
| 1000 | 120 $m^3$/d | 60 kg/d |

*Table 2: Average contamination of municipal wastewater [2]*

| Parameter | Specific polluting load (g/inh·d) | Average concentration for 120 l/inh per day (mg/l) |
|---|---|---|
| COD | 120 | 1000 |
| $BOD_5$ | 60 | 500 |
| N | 11 | 91,6 |
| P | 1,8 | 15 |
| Mixed liquor suspended solids | 70 | 583,3 |




*Picture 1: HUBER BioMem® Process*

The membrane's capacity for wastewater treatment determines the module number in VMR units. Therefore the VMR unit choice is case dependent.

$Q_{input}$ = 1000 inh * 120 l/inh · d = 120.000 l/d

120.000 l/d / 24 h = 5.000 l/h

5.000 l/h / 15 l · $m^2$/h = 333.33 $m^2$ · 1,1 = 366,6 $m^2$

The VMR unit operates with pauses, and multiplication by 1,1 is introduced.[2]

It has been calculated that the appropriate membrane area is 366,6 $m^2$ and the most suitable unit is VMR 20/120 (these figures represent the module number of the unit) with 5 $m^3$/h sewage volume and 360 $m^2$ membrane area.

## Aeration tank positioning

The aeration tank's shape and the contractor itself prevent sludge setting on the bottom of the tank. The contractor should be easily accessible for future maintenance. The tank should be 30 cm higher than the water level.

The volume of the basin for daily $BOD_5$ -fraction expressed in Bd (kg/d):

$V_{AT} = Bd_{BOD5} / (B_{SL} * SS_{BA})$ $m^3$ $V_{AT}$ - Useful capacity of the aeration tank [3]

$Bd_{BOD5}$ - Daily $BOD_5$-fraction

$B_{SL}$ - $BOD_5$- Sludge loading

$SS_{ST}$ - Mixed liquor suspended solids in the ac. sludge tank

Determination of the volume for the waste water treatment with sludge stabilization:

$B_{SL}$ < 0,07 kg/(kg·d) That corresponds to a sludge age from over 15 days. [4]

$SS_{ST}$ = 10 kg/ $m^3$ (8-12kg/ $m^3$ from Huber AG)

$Bd_{BOD5}$ = 1000 inh * 60 g/inh · d = 60 kg/d

$V_{AT}$ = 60 / (0,07 * 10) = 85,7 $m^3$

The aeration tank capacity should be greater than 85,7m3. VMR 20/120 has been chosen 2.536 mm in length and 2.300 mm wide, 2.700 mm submerged in water. VMR is set up with minimum 50 cm free space around it to allow mounting and maintenance. This shows that the tank must be 3,5 m long, 3,5 m wide, and 3,1 m high (2,7 m height of the VMR + 0,1 m beneath the water level, 0,3 m safe space). The aeration tank has the same length and width and if the tank volume is 85,7 $m^3$, its length is 8 m.

The needed amount of oxygen that is to be transferred in the wastewater to provide biological oxidation of the organic material is calculated by:

$\alpha OC = (O_O * Bd_{BOD5}) / 24$ kg/h  $\alpha$ OC - Oxygen transfer capacity in wastewater [5]

$O_O \geq 3,0$ kg/kg - Oxygen transfer capacity and $BOD_5$ -space loading

$Bd_{BOD5}$ = 60 kg/d

$\alpha OC$ = (3 * 60) / 24 = 7,5 kg/h

This amount is enough for oxidation of C and N under normal conditions.

The amount of oxygen transferred is calculated by:

$Q_V = \alpha OC / (f_{O2} * h_V)$ $m^3$/h  $f_{O2}$ = 8-10 g/$m^3$ - Specific utilization of oxygen [6]

$h_V$ = 2,8 m - Injecting depth of air in the water

$Q_V$ = 7,5 / (10 * $10^{-3}$ * 2,8) = 267,9 $m^3$/h

The amount of air current is 267,9 $m^3/h$. This can help us in calculating the investment costs.

## Results and discussion

To establish the overall investment costs (Table 3) first the individual costs should be calculated. This analysis will not take into account the operating costs because it is a small wastewater treatment plant and they are small. If needed, they can be added later on.

*Table 3: Investment cost*

| | Kind of the costs | Costs in Eur |
|---|---|---|
| 1 | Pipestrainer (mechanical treatment) | 16.910 |
| 2 | Collecting main basin, aeration and filtration tank [7] | 16.480 |
| 3 | Blowers, aerators, pump and pipework system for the aeration tank [8] | 5.000 |
| 4 | VRM- Vacuum Rotation Membrane | 114.100 |
| | Total | 152.490 |

The clarification process on municipal and industrial plants has been characterised by large space requirements, big structures, odour development and poor degradation and retention efficiency in case of varying loads. This results in a heavy environmental burden in the form of emissions and impairment of nature, high building costs and plant maintenance costs.

The HUBER membrane systems allow for size reduction of the structures required by up to 70 % and even increase the performance of wastewater treatment plants. Problems with scum or sludge overflow that occur with sedimentation are no longer an issue with filtration. Even existing structures can be retrofitted and the capacity increased. Existing preliminary and secondary clarification tanks can be modified and further used as storage and stand-by tanks.

## Conclusion

The effluent quality of such plants complies with all presently applicable standards and even allows direct reuse of the bacteria-free and germ-free effluent as service water (e.g. for irrigation). The benefits of HUBER BioMem® System are:

Modular and compact design;

Virtually unlimited combination of filtration and aeration units (grey and black water treatment);

Effective treatment and utilization of small wastewater flows;

No expensive sewer building costs;

Separation of all bacteria and virtually all germs;

Reuse of clarified wastewater as service water, cleaning water, toilet flushing water or for irrigation;

Effective removal of covering layers with a minimized energy demand through sequential cleaning of the membrane surfaces;

Frost-proof design for optional outdoor installation;

Suitable for optional underground installation.

## REFERENCES


[1] Prospekt – „Huber Membranbelebung VRM", Hans Huber AG, 1.2005

[2] Durchsatzleistung, Baugroße VRM 20, Datenpool, Hans Huber AG Status: 12.08.2005

[3] ATV-DVWK-Regelwerk: „ATV-A 122 Grundsätze für Bemessung, Bau und Betrieb von kleinen Kläranlagen mit aerober biologischer Reinigungsstufe für Anschlußwerte zwischen 50 und 500 Einwohnerwerten,,; Juni 1991; Copyright ATV-DVWK, Hennef 2003

[4] ATV-DVWK-Regelwerk: „ATV-A 126 Grundsätze für die Abwasserbehandlung in Kläranlagen nach dem Belebungsverfahren mit gemeinsamer Schlammstabilisierung bei Anschlußwerten zwischen 500 und 5000 Einwohnerwerten,,; Dezember 1993; Copyright ATV-DVWK, Hennef 2003

[5] ATV-DVWK-Regelwerk: „Arbeitsblatt A131,,; Bemessung von einstufige Belebungsanlagen; Mai 2000; Copyright ATV-DVWK, Hennef 2003

[6] ATV-Handbuch: „Biologische und weitergehende Abwasserreinigung" – 4. Auflage; Ernst & Sohn Verlag, Berlin, 1997

[7] Lange J., Otterpohl R.: „Abwasser – Handbuch zu einer zukunftsfähigen Wasserwirtschaft", Mall-Beton - Verlag Donaueschingen-Pfohren 1997

[8] Abwassertechnische Vereinigung e.V. in St. Augustin: „Lehr- und Handbuch der Abwassertechnik" – Dritte, überarbeitete Auflage; Verlag von Wilhelm Ernst & Sohn, Berlin/München, 1983

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E-mail: sitzams@eunet.rs
www.sitzam.org.rs

**ZA IZDAVAČA**
*Prof. dr MIOMIR PAVLOVIĆ, predsednik SITZAMS*

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*E-mail: karadzici@nadlanu.com*

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# HEAVY METALS IN WATERS ALONG THE RIVER BREGALNICA IN THE PART OF HYDROACUMULATION KALIMANCI TO KOCANI

Orce Spasovski[1], Trajce Mitev[1]

[1]*Faculty of Mining, Geology and Polytechnic, „Goce Delcev" University, Goce Delcev 89, MK-2000 Stip, Republic of Macedonia orce.spasovski@ugd.edu.mk, trajce.mitev@ugd.edu.mk*

## ABSTRACT

*In frame of this paper are given the results and findings from the research performed for determination of metal pollution in the flow of the river Bregalnica. After the analysis and interpretation of data were confirmed the assumptions for increased values of the the following metals: Zn, Pb, Cd, Cu, As and Ag. Since in the near vicinity is Sasa Mine for lead and zinc exploitation, especially interesting were the results for Pb that reached 0,019 mg/l, Zn that reached 0,029mg/l, Cd that reached 0,005mg/l, Ag that reached 0,056mg/l, As that reached 0,110 mg/l in waters. Increased concentrations of metals quite often were of several times magnitude over the maximal allowed standards. The increase of metals concentration was highest in the area of the hydroacumulation Kalimanci, and downwards through the flow of the river Bregalnica the concentrations decreased.*

***Key words:*** *heavy metals, pollution; lead; zinc; waters; Bregalnica River, Sasa Mine, maximal allowed concentrations.*

## INTRODUCTION

*Waste materials which are contained in the tailing of the hydro dump Sasa through the river Kamenicka are bring in the hydroacumulation Kalimanci. Water of the hydroacumulation Kalimanci is used for irrigation, and part of it flow into the river Bregalnica. Waste waters of the river Kamenicka, hydroacumulation Kalimanci and the river Bregalnica contaminate the land (sediments and soils), and also the underground waters accumulated in the wells which are located on the flow of the river Bregalnica.*

*The tailing which is disposed in the hydro dump Sasa is waste derived from the process of selective flotation concentration in which concentration of the lead and zinc minerals are concentrated. The composition of the waste materials is directly connected with the type and the quantity of the flotation reagents, characteristics of the processed ore, process of enrichment, and also pH value of the pulp. The liquid phase of the flotation tailing is composed of highly mineralized waste water with increased concentrations of sulphates, heavy metals, phenols and other toxic materials.*

Preliminary investigation results of this type can be found in the publications from (Mircovski, Spasovski at al. 2004, [1]; Spasovski at al. 2007, [2]; Spasovski, Doneva, 2007, [3][4]).

## GEOLOGICAL AND HYDRO GEOLOGICAL CHARACTERISTICS OF THE TERRAIN

The moving of the waste waters underground depends of the hydro geological characteristics of the terrain, which will be further present more detailed.

On the investigated terrain there are Quaternary alluvial sediments of the river Bregalnica and Neogene sediments in the vicinity of Kamenica and on the left side of the river Bregalnica in the vicinity of Kocani.

Alluvial sediments of the river Bregalnica consists of sands, gravel, and on some places sandy clays. This composition of the alluvial sediments made it possible accumulation of significant quantities of waste water with possibility of contamination of the sediments and soils.

Neogene sediments in the vicinity of Kamenica and on the left side of the river Bregalnica in the vicinity of Kocani are made of marly clays and Quaternary alluvial sediments presented by clays, sandy clays, sands and gravels.

There are open type wells on the investigated terrain with free level in which the level of underground water is near the surface. Good filtration coefficient and direct hydraulic connection with the river Bregalnica shows the possibility of contamination of the underground waters, sediments and soils with the waste waters from the hydro dump of the Sasa mine.

## Materials and methods

Preliminary field investigations were carried out in order to obtain essential data in the terrain. It included data on the Bregalnica River water courses slected as possible station for sample collection.

Samples from water flows and spring were collected in order to obtain data no the most critical points in terms of heavy metal contamination and how to direct future sampling and analyses.

Water samples werw collected below the flotation tailing pond whosw drainage waters flow into the Bregalnica River (fig. 1).The aim was to determine the effect that the mining activites and tailing pond have on the distribution of heavy and toxic metals in waters.

Water sampling was done with plastic syringe from the middle part of the water flow. The 50 ml of water from the syringe was transferred into a plastic vessel. It is of note when the water is transferred from the ssyringe to the vessel it is filtred through a paper filter the openings 45 μm. Acidizing with 0.4 ml of 50% nitric acid is done before closing the vessel. This is done to avoid settling of metals on the wall and bottom of the vessel.

The samples werw taken to laboratory for hemical analysis for heavy metal determination with AES-ICP.

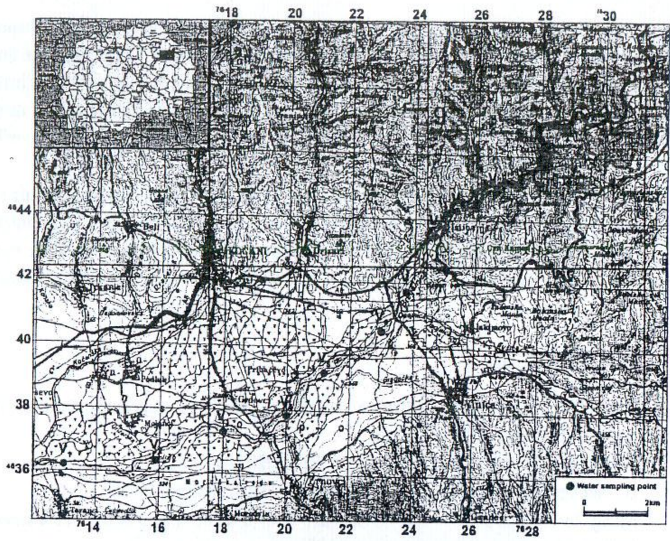


*Fig. 1. Topographic map with the sampling points*

## Results and discussion

The results obtained from flowing water samples are given in Table 1, with comparison between maximum allowable (MAC) concentracion of heavy and toxic metals for III – IV classes.

Data shown in Table 1 make it possible to define the amount of heavy metals in the Bregalnica River water and its tributaries and the reasons for their occurrence.

***Table 1.*** *Results of chemical analysis of sediments taken from the Bregalnica River and corresponding standards (mg/l), year 2007*

| | Pb | Zn | Cu | Cd | As | Ag | Fe | Mn |
|---|---|---|---|---|---|---|---|---|
| $V_1$ | 0,005 | 0,001 | 0,005 | 0,001 | 0,036 | 0,005 | 0.090 | 0,007 |
| $V_2$ | 0,007 | 0,001 | 0,005 | 0,002 | 0,064 | 0,003 | 0.088 | 0,007 |
| $V_3$ | 0,005 | 0,013 | 0,005 | 0,001 | 0,017 | 0,011 | 0,082 | 0,005 |
| $V_4$ | 0,005 | 0,002 | 0,009 | 0,002 | 0,043 | 0,003 | 0.087 | 0,007 |
| $V_5$ | 0,010 | 0,003 | 0,015 | 0,002 | 0,031 | 0,002 | 0,179 | 0,089 |
| $V_6$ | 0,015 | 01012 | 0,016 | 0,002 | 0,098 | 0,002 | 0.084 | 0,007 |
| $V_7$ | 0,015 | 0,112 | 0,018 | 0,005 | 0,076 | 0,007 | 0.084 | 0,008 |
| $V_8$ | 0,012 | 0,114 | 0,019 | 0,002 | 0,042 | 0,005 | 0.075 | 0,006 |
| $V_9$ | 0,017 | 0,124 | 0,010 | 0,002 | 0,060 | 0,002 | 0.095 | 0,110 |
| $V_{10}$ | 0,017 | 0,127 | 0,048 | 0,003 | 0,057 | 0,002 | 0.083 | 0,094 |
| $V_{11}$ | 0,019 | 0,118 | 0,039 | 0,002 | 0,072 | 0,008 | 0.077 | 0,009 |
| $V_{12}$ | 0,018 | 0,128 | 0,015 | 0,002 | 0,110 | 0,001 | 0.024 | 0,009 |
| $V_{13}$ | 0,019 | 0,129 | 0,019 | 0,001 | 0.099 | 0,056 | 0.029 | 0,015 |
| **Standard** | **0,01** | **0,1** | **0,01** | **0,0001** | **0,05** | **0,002** | **0.3** | **0,05** |

Based on the data presented in Table 1, certain constants can be given concerning the presence of particular hard metals in the waters of the river Bregalnica in a distance between the hydroacumulation Kalimanci to Kocani, as well as an opinion for the reasons which can contribute for the increased contents of particular metals.

The data for the concentration of zinc (Table 1) indicate its increased presence in most of the samples which were analyzed. The greatest concentrations of zinc are found in the sample $V_{13}$, which are 0.129 mg/l. The increased concentrations of zinc are also found in the samples: $V_{12}$, $V_{11}$, $V_{10}$, $V_9$, $V_8$, $V_7$ and $V_6$. In the remaining samples the concentration of zinc is present in amounts less than the standard ones. Generally, it can be concluded that the entire research area is contaminated with zinc. The increased concentrations of zinc are a result of the active working of the Mine for lead and zinc Sasa.

The increased concentration of lead are noticed in the samples $V_{13}$ (0,019 mg/l), $V_{12}$ (0,018 mg/l), $V_{11}$ (0,019 mg/l), $V_{10}$ (0,017 mg/l), $V_9$ (0,017 mg/l), $V_8$ (0,014 mg/l), $V_7$ (0,015 mg/l) and $V_6$ (0,015 mg/l). It is obvious that increased concentrations of lead are found in most of the samples, but the great sample concentrations of lead are found in those samples where increased concentrations of zinc were also found, which confirms the statement of the great influence of the hydro-waste dump and the active working of the Mines Sasa for the pollution of the environment with these metals.

In all the samples cadmium is found in extremely larger concentrations compared to maximum allowed concentration. The great sample concentrations of cadmium are noticed in the samples $V_7$ (0,005 mg/l) and $V_{10}$ (0,003 mg/l). This behavior of the cadmium is due to its geochemical characteristics (easily soluble, low mobility). The increased concentrations of cadmium follow the parts which are contaminated with zinc because it geochemically follows the minerals in the zinc.

The increased concentrations of copper are found in most of the samples, but the great sample concentrations of copper found in the samples $V_{10}$ (0,048 mg/l) and $V_{11}$ (0,039 mg/l), while in the remaining samples the concentrations of copper are close or less than in maximum allowed concentration. The presence of the copper in the waters of river Bregalnica is a result of the occurrence of chalkopyrite in an association with the minerals of the lead and zinc.

Arsenic is present in larger concentration in most of the analyzed samples, but especially larger concentration are noticed in the sample $V_{12}$ (0,110 mg/l). The increased concentrations of arsenic are a consequence of the occurrence of arsenic together with the minerals of the copper.

The received data for the silver (Table 1) points that the silver represents a contaminant for the entire drainage system of the river Bregalnica. The presence of silver is a result of the occurrence of native silver and minerals of silver in the Mines of lead and zinc Sasa.

Iron is present in concentrations lower than maximum allowed concentration and is not a significant contaminant of the drainage system of the river Bregalnica.

Attention should be paid for the high concentrations of the manganese in the samples: $V_9$ (0,110 mg/l), $V_{10}$ (0,094 mg/l) and $V_5$ (0,089 mg/l). The reason for the occurrence of the manganese in high concentrations in the waters of the river Bregalnica is a permanent hydro- waste dump in the direct environment of the hydroacumulation Kalimanci as a presence of the waste waters from the Mines Sasa.

## CONCLUSION

After summarizing all the facts which were received from this research, we could say that, due to the intensive mining in the Mine Sasa in the past few years, a serious disturbance of the natural metal balance was determined in mediums like waters. The results from the analysis of the samples taken from different points along river Bregalnica in a distance between the hydroacumulation Kalimanci to Kocani showed that this area is significantly contaminated with heavy metals and trace elements. The concentrations of the most of the elements in the waters are significantly larger closer to the hydroacumulation Kalimanci and they decrease with the distance.

The increased concentrations of the heavy and toxic metals are direct consequence of the following factors: geological composition of the area, anthropogenic influences such as mining, railing and deposition of tailing, physical-chemical features of waters (pH, Eh, etc.).

With the results and conclusions received from this analysis in the direct environment of the Mine Sasa the question remains open for the bioavailability of the determined metals and metalloids and the possibility of their inclusion in the food chain.

## REFERENCES

[1] **V., Spasovski, O., at al.** 2004: The disaster at the tailing pond of the Sasa lead and zinc mine and contamination of surface and underground waters. 5th International Symposium on Eastern Mediteranean Geology Thesaloniki, Greece, pp 1005-1007.

[2] **Spasovski, O., Dambov, R., Nikolova, M., Karanakova, R.,** 2007: Mine waters ot the Buchim deposit and the effect on the human environment. 2nd Balkan mining congress, Belgrade, Serbia.

[3] **Spasovski, O., Doneva, B.,** 2007: Heavy metals in the water of the river Zletovska and the vicinity. 2nd Balkan mining congress, Belgrade, Serbia.

[4] **Spasovski, O., Doneva, B.,** 2007: Heavy metals in sediments and soills along the river Bregalnica in the part of hydroacumulation Kalimanci to Kocani. Geologica Macedonica, pp 75-86.