

## HEAVY AND TOXIC METALS AND NUTRIENTS IN SEPARATE PLACES IN THE RIVER BREGALNICA, (EASTERN MACEDONIA)

*Orce Spasovski*

*Faculty of Natural and Technical Sciences, University "Goce Delchev" – Stip, Goce Delchev 89 MK-2000, Stip, Republic of Macedonia, orce.spasovski@ugd.edu.mk*

**ABSTRACT.** Through a small scale of geochemical and geoeological research through the flow of the river Bregalnica, this paper will present the information about the character of the waters of the river, the level of presence of hard and toxic metals, nutrients and the amount of organic contamination. These researches will define the condition and the presence of Fe, Mn, Pb, Zn, Cd, Cr, Co, Cu, cyanides, detergents, organic contaminators in separate measurement locations through the flow of the river Bregalnica.

During the realization of these researches, the first thing was the approach to determine the required geochemical monitoring through the flow of the river Bregalnica. When the conditions of the waters of the river Bregalnica are considered from the aspect of presence of hard and toxic metals, it can be stated that all the measured parameters are under the allowed concentrations with the exception of Arsenic and Manganum which showed higher concentrations in separate measurement locations.

Key words: heavy and toxic metals, cyanides, nutrients, organic contaminators, river Bregalnica.

### ТЕЖКИ И ТОКСИЧНИ МЕТАЛИ И ХРАНИТЕЛНИ ВЕЩЕСТВА В РАЗЛИЧНИ ТОЧКИ НА РЕКА БРЕГАЛНИЦА, ИЗТОЧНА МАКЕДОНИЈА

*Орче Спасовски*

*Универзитет "Гоце Делчев", Штип, Факултет по естествени и технички науки*

**РЕЗЮМЕ.** Докладът представя информация за водите на р. Брегалница, съдържанието на тежки и токсични метали, хранителни вещества и количеството на органични замърсители в резултат на геохимични и геоокологични изследвания.

Изследванията установяват наличието на Fe, Mn, Pb, Zn, Cd, Cr, Co, Cu, цианиди, почистващи препарати и органични замърсители в отделни точки по поречието на р. Брегалница. След като бяха взети предвид всички данни за наличието на тежки и токсични метали, бе установено, че измерените параметри са под допустимите стойности, с изключение на арсен и манган, които показаха по-високи концентрации в отделни точки.

**Ключови думи:** тежки и токсични метали, цианиди, хранителни вещества, органични замърсители, р. Брегалница.

#### INTRODUCTION

The river Bregalnica flows through the valley in Kocani and after leaving Stip it enters the river Vardar (figure 1 and 2). The quality of the river is classified with class 3. In its flow under the town Stip, there are disrupted physical and organoleptic properties of the water with a high level of suspended substances and microbiological contamination is on a maximum level. This is a result of the drainage of sewage from the households, the collection system and the industry.

The main industrial capacities from the territory of the town Stip are the textile factories, the meat processing industry, factory for production of edible oil, poultry farm, pigs farm, etc.

The industrial sewage is partly released in the collection system and partly in directly into the rivers.

#### METHODOLOGY OF RESEARCH

In order to achieve the desired goal, the initial approach was to establish the required geochemical monitoring through the flow of the river Bregalnica and geochemical points were

established on the bank of the river Bregalnica in several points: close to the village Istibanja, under the village Orizari, under the town Kocani, at the point of river Zletovica in Bregalnica, under the village Karbinci, at a point where it enters Stip, at a point where it leaves Stip, at the approximate proximity of the entrance of the river Bregalnica at the river Vardar. (figure 2)

Samples of the waters were collected at the pointed measurements points for performing further laboratory researches.

The samples that were collected were divided into two parts, one of which was preserved in a place with HNO<sub>3</sub>, and the other part was not preserved and was treated immediately in a laboratory from an aspect of determining the elements of the organic contamination.

During the laboratory researches several methods were used: the method of inductively coupled plasma (ICP-AES), then spectrophotometric methods (UVE-VIS), volumetric and gravimetric methods.



Fig.1. Map of the Republic of Macedonia with location of investigated area

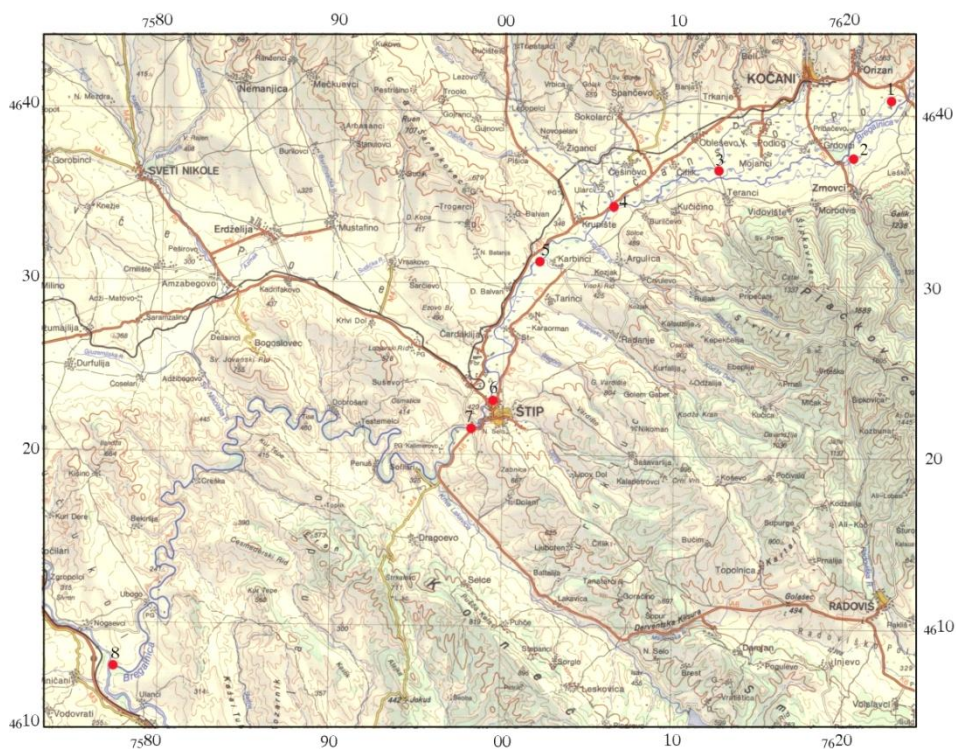


Fig. 2. Typographic map with specified places of the taken samples

#### RECEIVED RESULTS AND COMMENT

From the received results it can be stated that the value of BOD in the waters of Bregalnica is between the range of 3.8 to 5.8 mgO<sub>2</sub>/l and the value of COD is between the range of 17.2 to 21.2 mgO<sub>2</sub>/l. If we compare these results to the values of BOD and COD in the rivers in Europe we can come to the

conclusion that these values integrate with the 75% of the values from the rivers of Europe which have values of BOD of 4.7 mgO<sub>2</sub>/l and values of COD of 25 mgO<sub>2</sub>/l. From this perspective we can conclude that the river Bregalnica is among the rivers which are relatively polluted with organic contamination substances and as such is integrated in the

percentage of contamination present in 75% of the rivers in Europe. These contaminations are primarily caused by the urbanization of the towns that are situated near the flow of the river Bregalnica and they are a product of the industrial and urban waste which come from the industrial and city zones of the towns.

Table 1.

The concentration of heavy and toxic metals in separate places in the river Bregalnica and the presence of organic contaminators and nutrients (in mg/l)

| Elements  | Sample № |        |       |        |       |        |        |        |
|-----------|----------|--------|-------|--------|-------|--------|--------|--------|
|           | 1        | 2      | 3     | 4      | 5     | 6      | 7      | 8      |
| Ca        | 62.53    | 60.11  | 60.28 | 58.5   | 65.31 | 48.56  | 48.65  | 31.25  |
| Mg        | 17.89    | 16.32  | 15.87 | 14.56  | 15.21 | 13.25  | 14.52  | 8.95   |
| Na        | 23.65    | 19.54  | 17.65 | 17.85  | 15.32 | 14.52  | 18.65  | 6.54   |
| K         | 3.21     | 2.85   | 3.65  | 2.65   | 2.85  | 1.65   | 2.54   | 1.45   |
| Al        | 0.421    | 0.451  | 0.421 | 0.431  | 0.465 | 0.356  | 0.354  | 0.254  |
| Fe        | 0.385    | 0.421  | 0.235 | 0.231  | 0.256 | 0.589  | 0.265  | 0.05   |
| Mn        | 0.264    | 0.021  | 0.254 | 0.324  | 0.178 | 0.487  | 0.028  | 0.023  |
| P         | 0.185    | 0.065  | 0.042 | 0.065  | 0.035 | 0.065  | 0.051  | 0.05   |
| Sr        | 0.354    | 0.381  | 0.365 | 0.387  | 0.398 | 0.254  | 0.381  | 0.187  |
| Ni        | 0.003    | 0.006  | 0.041 | 0.007  | 0.002 | 0.005  | 0.003  | 0.001  |
| Co        | 0.0068   | 0.0054 | 0.003 | 0.001  | 0.002 | 0.002  | 0.002  | 0.003  |
| Cr        | 0.001    | 0.001  | 0.001 | 0.003  | 0.001 | 0.001  | 0.001  | 0.001  |
| Zn        | 0.005    | 0.006  | 0.005 | 0.005  | 0.006 | 0.009  | 0.006  | 0.005  |
| Cu        | 0.005    | 0.007  | 0.007 | 0.008  | 0.001 | 0.001  | 0.006  | 0.03   |
| Pb        | 0.005    | 0.005  | 0.001 | 0.002  | 0.004 | 0.005  | 0.005  | 0.005  |
| Cd        | 0.002    | 0.001  | 0.001 | 0.001  | 0.001 | 0.001  | 0.001  | 0.001  |
| As        | 0.058    | 0.038  | 0.035 | 0.001  | 0.032 | 0.065  | 0.051  | 0.045  |
| Mo        | 0.021    | 0.001  | 0.001 | 0.0354 | 0.008 | 0.0187 | 0.0004 | 0.0232 |
| W         | 0.0421   | 0.0154 | 0.005 | 0.005  | 0.005 | 0.0256 | 0.0187 | 0.005  |
| V         | 0.05     | 0.048  | 0.065 | 0.045  | 0.052 | 0.025  | 0.032  | 0.031  |
| Ag        | 0.001    | 0.001  | 0.001 | 0.002  | 0.001 | 0.001  | 0.001  | 0.001  |
| NO3-      | 6.2      | 4.8    | 6.8   | 1.5    | 2.5   | 3.2    | 4.5    | 1.1    |
| NO2-      | 0.1      | 0.5    | 0.05  | 0.05   | 0.06  | 0.09   | 0.08   | 0.9    |
| NH4+      | 0.05     | 0.21   | 0.04  | 0.04   | 0.05  | 0.08   | 0.04   | 0.06   |
| SO42-     | 46.2     | 38.6   | 36.2  | 68     | 45.2  | 45.2   | 56.3   | 38.5   |
| cyanide   | 0        | 0      | 0     | 0      | 0     | 0      | 0      | 0      |
| Detergent | 0        | 0      | 0     | 0      | 0     | 0      | 0      | 0      |
| pH        | 7.7      | 7.8    | 7.8   | 7.8    | 7.8   | 7.8    | 7.7    | 7.8    |
| BOD       | 4.2      | 4.5    | 4.4   | 5.8    | 4.4   | 3.6    | 5.1    | 3.8    |
| COD       | 19.8     | 19.3   | 17.5  | 17.5   | 18.3  | 21.2   | 20.3   | 17.2   |

The cyanides and detergents have not been found in the researches of the waters of river Bregalnica and in relation to the pH values of the character of the waters it can be stated that there are no phenomena of acidity in the environment and the waters of the river are with standard pH values. From the presented data in the Table it can be stated that almost all

analyzed elements in the waters are within the allowed concentration ranges with the exception of phosphorus which is increased in all analyzed samples in the scale of its allowed concentration of 0,1 mg/l and the increased content of Arsenic in the samples from the localities 1, 3, 4, 5 in the scale of its allowed concentration of 0,05 mg/l.

## Conclusion

Taking into consideration all the researches in respect of the conditions of the waters of the river Bregalnica from the aspect of presence of heavy and toxic metals, it can be stated that all measured parametars are under the allowed concentrations with the exception of Arsenic and Manganum which appeared to be present in increased concentrations in certain measuring places.

The condition of the organic contaminators and nutrients basically prescribe the need of more detailed researches of this problem through maintaining a permanent monitoring of the running waters of the river Bregalnica as well as the permanent monitoring of the waste waters in the town places through the flow of the river Bregalnica.

It should be mentioned that it would be advisable some finances to be provided for establishing automatic control stations for the quality of the running waters of the river Bregalnica and in the shortest period of time a cadastre/register to be prepared for the contaminators of the waters of river Bregalnica with detailed acts for the waste materials which go into the river from the industrial objects and the communal field.

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