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Original scientific paper

EXAMINATION OF HEAVY AND TOXIC METALS IN THE KOZJAK LAKE AND TRESKA RIVER WITH PROTECTION MEASURES

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A b s t r a c t: The aim of our study was to examine the situation with heavy metals in water and stream sediment of Kozjak lake and Treska river, and to recommend measures to prevent pollution. Water quality and sediment was examined of aspect of the content of six very important chemical elements known as heavy and toxic metals, including: lead (Pb), cadmium (Cd), chromium (Cr), iron (Fe), copper (Cu) and arsenic (As). Modern methods of laboratory testing of chemical elements were applied: Atomic absorption spectroscopy, atomic emission spectrometry method with double plasma (AES-ICP) method and the atomic absorption spectrometry electro thermal (ETAAS). Total of 120 samples were analyzed in water and 48 samples in stream sediments. The paper will also indicate measures to protect the Kozjak lake and Treska river from possible contamination. Especially significant role for Kozjak Lake was building the Dam for production of electricity HPP "Kozjak", which is the biggest artificial dam in the country. But despite this, the Kozjak lake already used as protection from floods Skopje, fishing, еко-lake tourism but need to think and plan about using for potable water for irrigation of crops, but also as an alternative water supply of the city of Skopje.

Key words: Kozjak lake; Treska river; heavy metals

INTRODUCTION

Accumulation "Kozjak" is the largest artificial lake, in depth and in length in the country, and also in the total amount of water in it. The Kozjak lake is located on the Treska river, 15 km from the opposite of Matka Dam (Fig. 1). The length of the lake is 33 km.

Republic of Macedonia as a candidate member of the European Union is obliged to meet all the standards for the protection and improvement of the environment. The current process of accession to the European Union requires effective water management, throe the Water Act which enshrined the Water Framework Directive (Directive 2000/60/EC), Directive drainage and waste water treatment (91/271/EEC), Directive for the water intended for drinking (98/83/EEC), Directive for treatment of sludge (86/278/EEC) and others. Macedonia aspires to join the EU in the near future, and expects to start negotiations for EU integration.

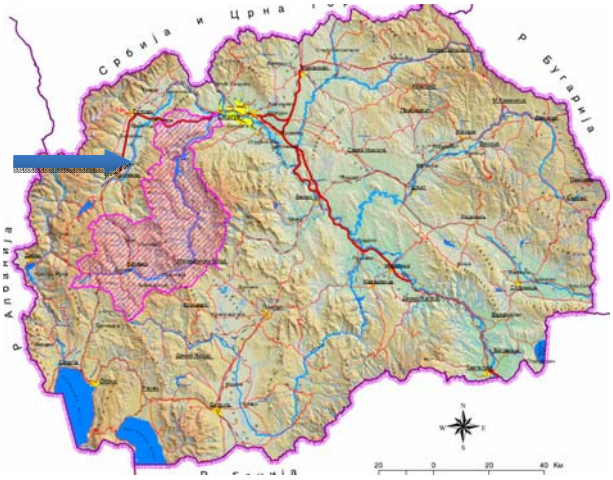

Fig. 1. Geographical location of the research area

The water resource imposes the need for development planning approach, promotion and protection of water resources, certainly within the

Spatial Plan of the Republic of Macedonia and the Spatial Plan of the region at the confluence of the Treska river.

The management of water resources requires interdisciplinary approach, which means more engagement shots from a number of specialties, including engineers of Environmental Protection, hydrologists, geologists, technologists, agronomists, civil engineers, economists and others.

In the above context, this paper will be included in a segment research approach to water accumulation on the artificial Kozjak lake (specifically, the content of some heavy and toxic metals in the lake water, lake sediments, in water and sediments at Treska river, as the main power source of the Kozjak lake). The are no any literature data from the previous studies for heavy metals in Kozjak lake and Treska river.

RESEARCH AREA

The purpose of the research is to ascertain the state of water quality in the Kozjak lake and Treska river in terms of representation of toxic heavy metals that were subject to our task and goal in the study, and thus assessing the quality of the water of Kozjak lake and Treska river.

The territory of the catchment area of the Treska river in the census of 2002 has 101,392 inhabitants. The catchment area of the Treska river concentrated 11.1% of the forests in the state. The total catchment area of the Treska river, 209 500 ha of forests and forest land represented an area of 127,147 ha.

An estimated quantity of wastewater will amount Q_{sr}/year = 9,869,600 m^3/year, or specific biological contamination will be BPK_5/year = 2643330 kg BPK_5/d. The hydrographic network of the Treska river is very developed in the upper part of the water flow. In the boundaries of the observed area (Kozjak–Belička River) flowing three major waterways: Mala reka river left bank of the river Belica and Oča from the right bank. Larger right tributaries of Mala reka river are: the left bank – Poduška, Čhečen, smithing, Petrova and Unečka river and the right bank Trenkovska river. According to the spatial dispersion of industrial facilities by municipalities belonging to the region of the confluence of the Treska river, industrial activity is concentrated in the area of municipal Kičevo, Oslomej and Makedonski Brod. The remaining space is characterized by underdevelopment, backwardness and even the areas where the main activity is extensive agriculture and livestock.

Region of the reservoir "Kozjak" represents a specific spatial and functional whole ambience, which has features of special micro within the broader Porečje as in framework of administrative area of the municipality of Samokov. The scope of the plan of the region of accumulation "Kozjak" has a total area of 25.510 ha, occupies the space between the mountains of Karadzica, Jakupica and Dautica east, north of Suva Gora, west of Dobra Voda and south from Bušava Planina and Sač.

Hydropower plant "Treska" is designed and constructed with installed capacity of 50 MW and an annual production of 150 GWh. The power house is located at the foot of the dam.

Accumulation "Kozjak" formed by the construction of stone dam, located in the canyon of the Treska river, about 16 km from the existing dam of "Matka" and about 22 km from the estuary of the Treska river into Vardar river.

According to the strategic documents, the purpose of accumulation "Kozjak" and it is versatile: the protection of the downstream area from flooding, provide water for drinking of city of Skopje, irrigation of "Skopsko Pole" and energy production.

METHODOLOGY

For a detailed review of the field used satellite maps of the river basin of Treska and Kozjak lake. In accordance with the analyzes and checking on the ground, we conclude that the subject of research on Kozjak lake will be four locations for taking samples (Fig. 2), as follows:

- Location 1: the dam Kozjak
- Location 2: the village of Zdunje
- Location 3: the village of Blizansko
- Location 4: at the confluence of the Treska river in Kozjak lake.

From these four locations took water samples from two depths, and that first rehearsal:

• 20 cm under the water level,

• a second depth from the bottom of the Kozjak lake.

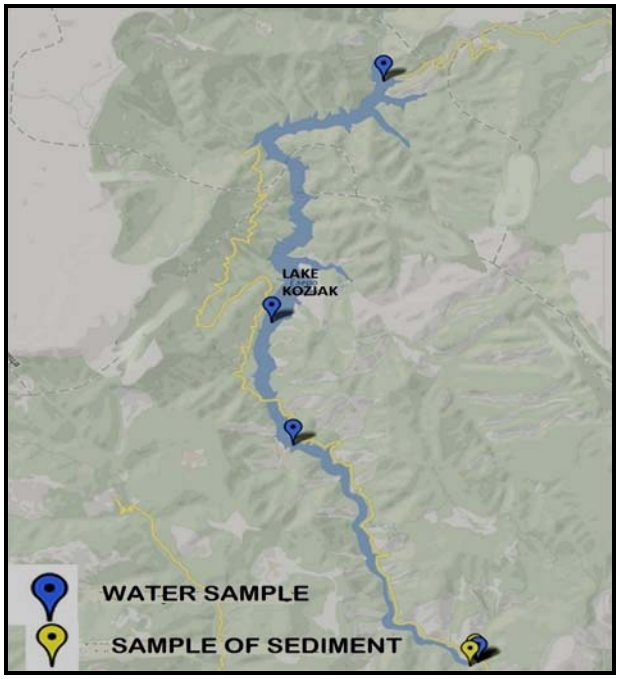

Fig. 2. Locations of sampling taken on water and sediment from Kozjak lake

Samples of sediment are taken only in site number 4 and the left and right bank of the Kozjak lake.

Rehearsals are taken in two periods of the year, and this at a time when the water level of rivers and lakes is small – October 2012, and when the water level of rivers and lakes is high – April 2013.

As an additional activity of this paper conclude that it is necessary to take samples of the water and sediment in the whole course of the Treska river, and for this purpose during the period when the water level of rivers and lakes is high in the month of April 2013, we took water and sediment at 4 locations on the Treska river, including:

• the source of the Treska river

• Treska river after Kičevo

• Treska river after Makedonski Brod

• Treska river after village of Belica.

The sampling of water was taken with standard MKC EN ISO 5667-6. The survey was carried out of the water in an accredited laboratory (Center for Sanitary Control) for Water Supply and Sanitation – Skopje.

T a b l e 1

GPS Locations of taken sampling

Location	GPS position	
Near the dam	41.874690	21.194193
Village of Zdunje	41.800639	21.157608
Village of Blizansko	41.761085	21.165762
Treska river flows into Kozjak lake	41.695002	21.222024
Source Treska river	41.47798	20.81822
Treska river after bridge Kičevo	41.47896	20.98852
Treska river after M. Brod	41.52937	21.23743
Treska river in Belica	41.67716	21.25210

Fig. 3. Taking samples from Kozjak lake

The analysis of heavy metals in water was performed by: Atomic absorption spectroscopy. Examination of heavy metals in sediment were performed in the accredited laboratory within the Department of Plant Protection and Environment Faculty of Agriculture, University "Goce Delčev" – Štip. Elements are analyzed by exploring the application of atomic emission spectrometric method coupled plasma (AES-ICP) method and the atomic absorption spectrometry electrothermal (ETAAS).

RESULTS AND DISCUSSION

The methodology applied to the analyses of the water and stream sediment samples basically includes:

- samples of water and sediment;
- preparation of the samples;
- identification of the presence of macroelements and trace elements in water and sediment through the method ICP-AES and ETAAS;
- interpretation of the obtained results.

The sampling of water was taken with standard MKC EN ISO 5667-6.

For obtaining more accurate results, the preparation of the samples was made with utmost precision and care. The sediment samples for the analysis with ICP-AES method were prepared in phases as follows:

- we dried the sediments specimens in dry premises;
- in porcelain dish and with grinding machine;
- we pressed the samples in order to obtain are presentative sample for laboratory analysis;
- we dissolved the samples in order to be able consequently to determine the elements of the ICP-AES instrument.

These are the elements that was analyzed and identified with the ICP-AES and ETAAS: lead (Pb), cadmium (Cd), chromium (Cr), iron (Fe), copper (Cu) and arsenic (As).

Interpretation of the obtained results

Macro-elements in samples of water and sedimnets were determined using ICP-AES and ETAAS in Kozjak lake. Obtained results for total concentration of 6 elements in samples of water and sediments are given in Tables 1, 2 and 3.

In conjunction with analyzes of water in Kozjak lake in both periods 10.10.2012 and 19.04.2013, in addition we present significant results presented through graphs for heavy metals: Fe, As, Pb, Cu, Cd (Figs. 4a,b,c,d).

Table 1

Obtained results of analysis of heavy metals in water accumulation Kozjak 10.10.2012 (μg/l)

Loaction	Near the dam	Near the dam	Village Blizansko	Village Blizansko	Village Zdunje	Village Zdunje	Treska river flows into Kozjak lake	Treska river flows into Kozjak lake
Depth	20 cm	50 m	20cm	30 m	20 cm	38 m	20 cm	7 m
Heavy metals								
Fe	–	5.907	0.863	15.0	–	19.5	1.30	6.01
As	–	0.259	–	–	–	0.358	–	1.34
Cr	0.438	0.435	0.221	–	0.046	0.132	–	–
Pb	–	–	–	–	–	–	–	–
Cd	–	–	–	–	–	–	–	–
Cu	–	–	–	–	–	–	–	–

Table 2

Obtained results of analysis of heavy metals in water accumulation Kozjak 19.04.2013 (μg/l)

Loaction	Near the dam	Near the dam	Village Blizansko	Village Blizansko	Village Zdunje	Village Zdunje	Treska river flows into Kozjak lake	Treska river flows into Kozjak lake
Depth	20 cm	50 m	20 cm	50 m	20 cm	29 m	20 cm	22 m
Heavy metals								
Fe	4.507	8.804	27.63	25.27	44.63	68.00	61.94	90.53
As	1.043	0.643	0.439	0.521	0.713	0.421	0.316	0.780
Cr	2.353	0,001	–	–	–	–	–	–
Pb	1.623	1.127	0.643	0.897	1.086	0.622	1.035	0.570
Cd	0.186	0,060	0.186	0.053	0.050	0.100	0.002	–
Cu	4.356	4.220	2.292	3.199	4.276	2.669	3.258	2.055

Table 3

Obtained results of analysis of heavy metals in sediment in Kozjak lake (mg/kg)

Loaction and date	Left coast Kozjak lake 10.10.2012	Right coast Kozjak lake 10.10.2012	Left coast Kozjak lake 19.04.2013	Right coast Kozjak lake 19.04.2013
Fe	1.56	1.65	2.7	1.7
As	11.5	11.5	10.3	9.2
Cr	10	40	72	46.3
Pb	17.1	18	26.4	28.9
Cd	0.33	0.32	0.34	0.27
Cu	15.2	16.3	17.5	21.1

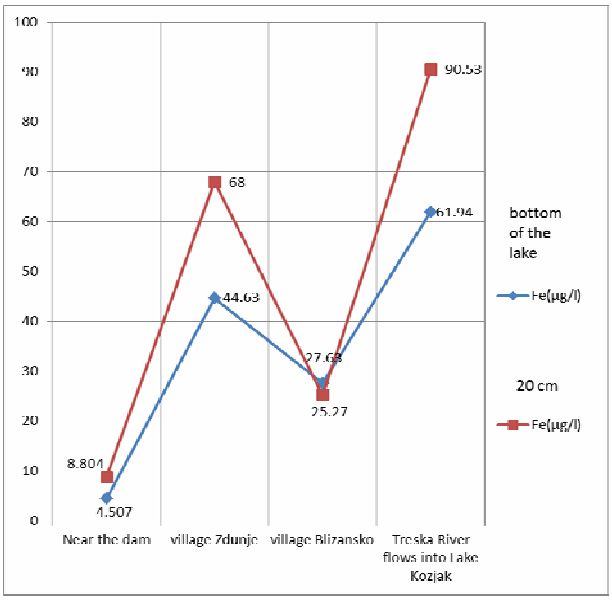

Fig. 4a. Concentration of iron (Fe) in all 4 locations of two depths (19. 04. 2013)

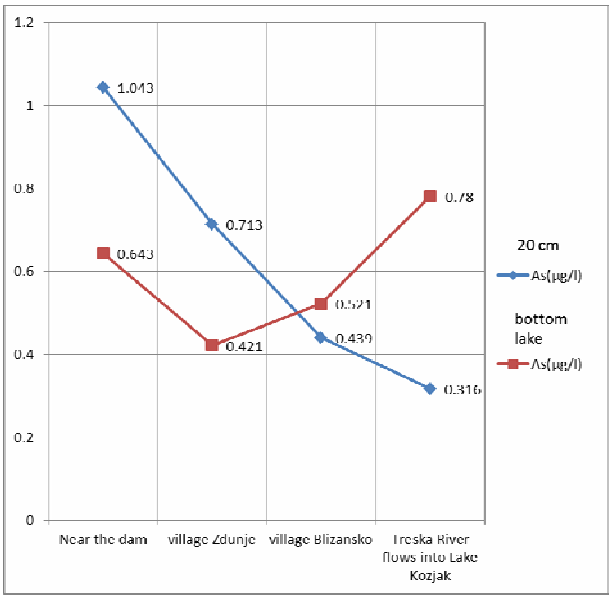

Fig. 4b. Concentration of arsenic (As) in all 4 locations of two depths (19. 04. 2013)

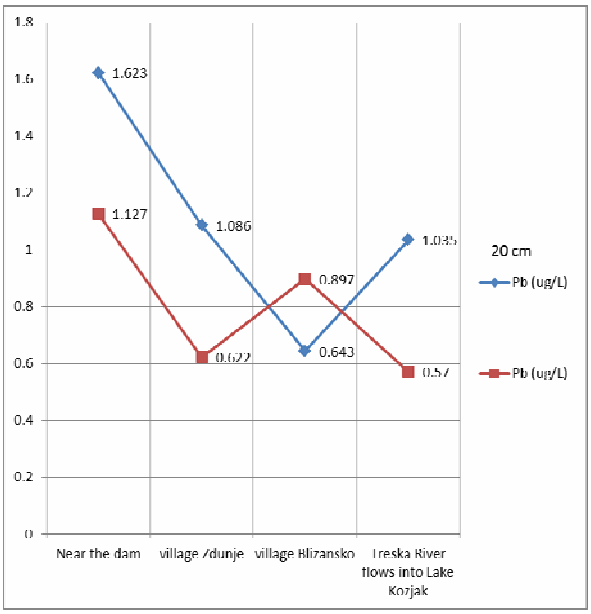

Fig. 4c. Concentration of lead (Pb) in all 4 locations of two depths (19. 04. 2013)

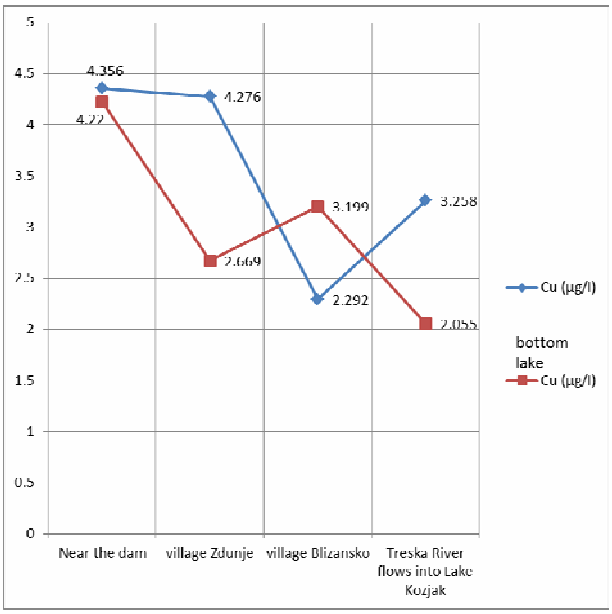

Fig. 4d) Concentration of copper (Cu) in all 4 locations of two depths (19. 04. 2013)

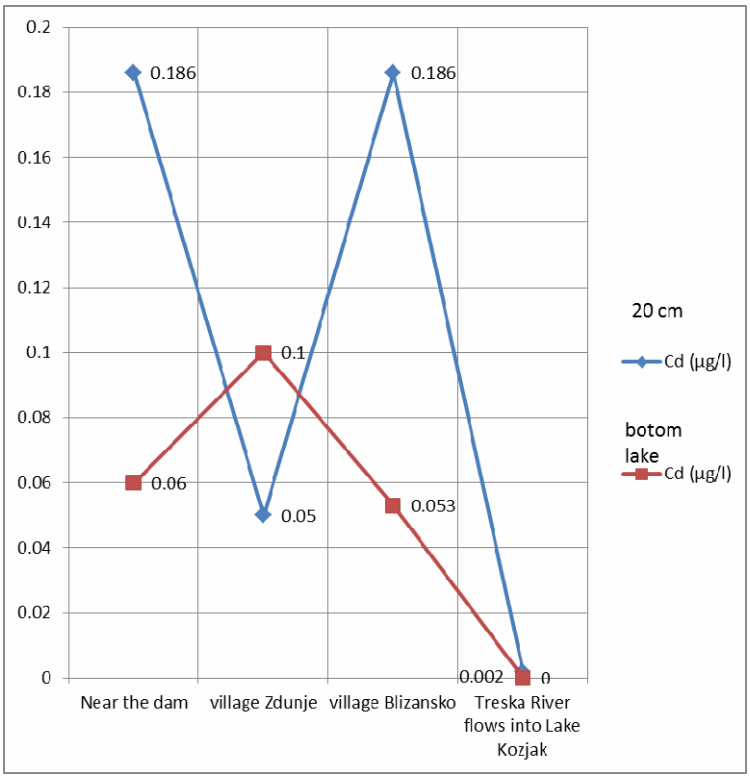

Fig. 4e. Concentration of cadmium (Cd) of all 4 locations of two depths (19. 04. 2013)

Comment on the results of heavy and toxic metals in waterand sediments in Kozjak lake

• Height difference between the period of autumn and spring in the Kozjak lake is 7.8 meters.

• Samples of water taken in the autumn of the year showed significantly lower values or quantities of toxic heavy metals, compared with samples taken in the spring of the year

• In two location in dam Kozjak and village Blizansko quantities for cadmium are above MDK for first and second class water element.

• Interpretation greater flow of water from the catchment area of the Treska river, through autumn, winter and spring is significantly larger, and thus more input heavy toxic elements in the lake.

• Contents of heavy and toxic metals in sediment accumulation Kozjak not exceeded MDK values compared to Dutch standards for soil quality. Let us mention that these stream sediment samples taken from the surface level of the lake near the mouth of the river treska at Kozjak lake, that does not mean that they would be identical to the samples if they were taken from the bottom of the Kozjak lake. But it will require more extensive analysis and proper equipment for taking sediment from the lake bottom.

2. RESULTS OF EXAMINATION OF HEAVY AND TOXIC METALS IN WATER IN TRESKA RIVER

Macro-elements in samples of water and sediments were determined using ICP-AES and ETAAS in Treska river. Obtained results for total concentration of 6 elements in samples of water and sediment are given in Table 4 and 5.

In conjunction with analyzes of water in Treska river in 20.04.2013, in addition we present significant results presented through graphs for heavy metals Fe, As, Pb, Cd in 4 locations (Fig. 5):

Comment on the results of heavy and toxic metals in water and sediment in the Treska river

• For all tested heavy metals are showing an increasing trend from the Treska river to Kozjak lake.

• The elements As, Cr, Pb in sediments of the Treska river has significantly at high volumes compared to water. Yet all three chemical elements

under maximum concentration limits for sediment, according to Dutch standards.

• The state of cadmium in Treska river is significantly increased in the locality Makdonski Brod, and the site Belica. The stated amounts are higher for water first and second class compared with the MDK.

Measures for protection of Treska river and Kozjak lake

Based on the prepared "Feasibility study for the disposal of wastewater from Kičevo microregion", (Feasibility study wastewater disposal from Kicevo microregion 2011) experts recommend treatment of wastewater with planned construction of a collection system, the length of 65 kilometers and three wastewater treatment plants (Kičevo Popovjani and Plasnica). The construction of this system for wastewater treatment in microregin creates conditions to prevent further environmental contamination in residential areas, will increase the level of cleanliness of the Treska river, and thus the Kozjak lake.

• It increased inspection on A and B integrated environmental permit Treska region.

• The planned weekend settlements along the Kozjak lake, need to build a collection system and a system for waste management.

• Under urgently needed remediation and landfill dislocation Kičevo.

• The using of IPA funds in real terms to finance infrastructure projects in this region.

Table 4

Obtained results of analysis of heavy metals in water of the Treska river 20.04.2013 (μg/l)

Location in Treska river	Source Treska river	Treska river after bridge Kičevo	Treska river after M. Brod	Treska river in Belica
Depth	Surface water			
Heavy metals				
Fe	8.856	24.57	59.72	62.50
As	0.426	0.539	0.468	0.654
Cr	–	–	–	–
Pb	0.012	0.463	0.091	0.542
Cd	0.033	0.052	0.179	0.472
Cu	1.416	1.319	1.642	1.691

Table 5

Obtained results of analysis of heavy metals in sediments in Treska river 20.04.2013

Location	Source Treska river	Treska Riv er after bridge Kicevo	Treska river after M. Brod	Treska river in Belica
Heavy metals	Sediments (mg–kg)			
Fe	2.90	4.20	4,00	3.80
As	4.70	25.5	16.10	19.70
Cr	84.10	71.10	64.50	72.70
Pb	17.50	21.40	20.60	23.30
Cd	0.57	<0.10	<0.10	0.39
Cu	24.20	28,00	19.80	25.10

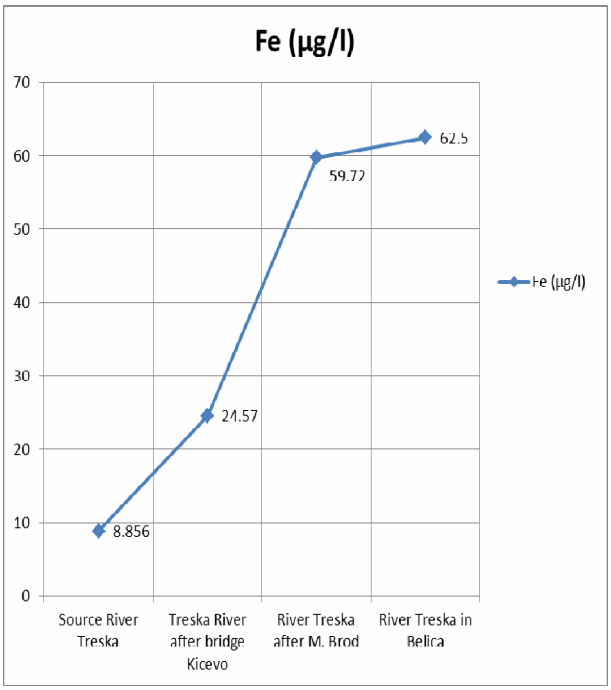

Fig. 5a. Content of iron (Fe) in water at 4 locations on Treska river

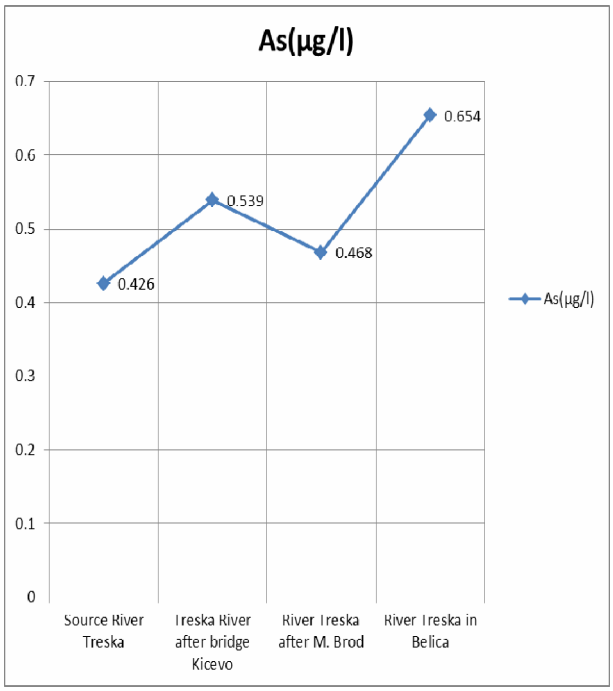

Fig. 5b. Contents of arsenic (As) in water at 4 locations on Treska river

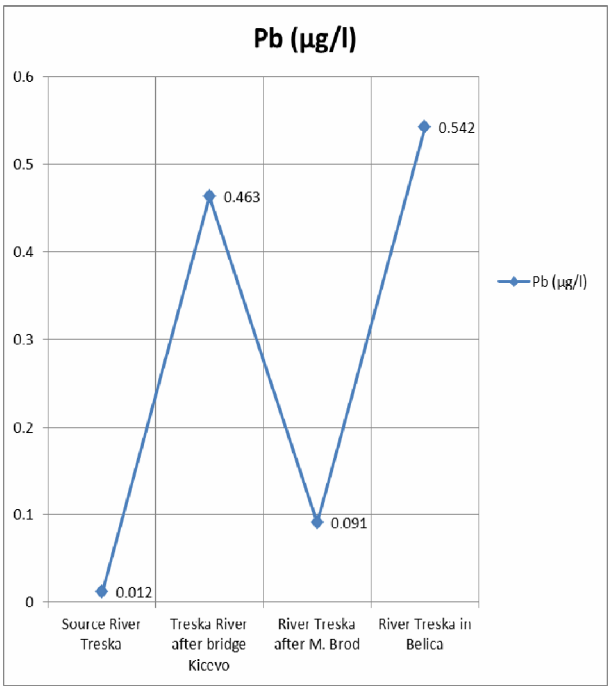

Fig. 5c. Contents of lead (Pb) in water at 4 locations on Treska river

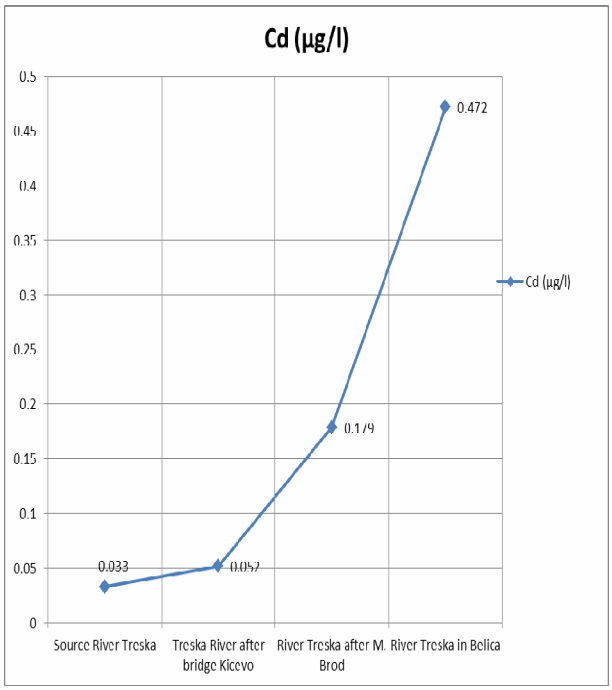

Fig. 5d. Contents of cadmium (Cd) in water at 4 locations on Treska river

CONCLUSION

Within this paper were examined 8 locations (4 in Kozjak lake, 4 on Treska river), and 6 were analyzed toxic heavy metals : lead, cadmium, chromium, arsenic, copper and iron. Total of 120 samples were analyzed in water and 48 samples in stream sediments. Collected water samples were analyzed by atomic absorption spectroscopy Perkin Elmer AA 700 – AA 800 and porters of sediment

were analyzed by atomic emission spectrometry method coupled plasma (AES-ICP). Results of analyzes of water were compared with the Regulation on classification waters of March 23, 1999. Deviations were found in two locations in samples of water, in the dam Kozjak and village of Blizansko quantities above MPC for element cadmium for first and second class water. Also found deviations of cadmium from the first and second class of water in the Treska river site Makedonski Brod site in the village of Belica.

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Р е з и м е

ИСПИТУВАЊЕ НА ТЕШКИ И ТОКСИЧНИ МЕТАЛИ ВО ЕЗЕРОТО КОЗЈАК И МЕРКИ ЗА ЗАШТИТА

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Клучни зборови: езеро Козјак; река Треска; тешки метали

Целта на нашето истражување беше да ја испитаме состојбата со тешки метали во водата и стрим-седиментот во езерото Козјак и реката Треска и да препорачаме мерки за заштита од загадување.

Квалитетот на водите и седиментот го испитувавме од аспект на содржината на шест мошне значајни хемиски елементи, познати како тешки и токсични метали, и тоа: олово (Pb), кадмиум (Cd), хром (Cr), железо (Fe), бакар (Cu) и арсен (As). Применивме современ метод за лабораториско испитување на хемиските елементи: атомска апсорпциона спектроскопија, атомски емисионен спектрометриски метод со двојна плазма (AES-ICP) и метод на електротермална спектрометриска атомска апсорпција (ETAAS). Вкупно беа анализирани 120 проби вода и 48 проби стрим-едимент.

Во трудот се посочуваат исто така и мерки за заштита на езерото Козјак и реката Треска од можни контаминации. Особено значајна улога на езерото Козјак има изградена брана за производство на електрична енергија ХЕЦ „Козјак“, која е најголема вештачка брана во Република Македонија. Но, покрај тоа, езерото Козјак веќе се користи и како заштита на Скопје од поплави, за риболов и езерски туризам, а е потребно да се размисли и планира и за користење технолошка вода, за наводнување на земјоделски култури, но и како алтернатива за водоснабдување на градот Скопје.