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Assessment of Toxic Metal Pollution in Some Rivers in the Tikveš Basin, Republic of Macedonia

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***Abstract*- The Tikveš Basin, which covers the central and the south parts of the Republic of Macedonia, boasts a favourable geographic location and is of distinctive strategic and economic importance for the country. The region, however, has modest hydrological resources and faces a series of accumulated water management problems that hugely affect water supply, erosive processes and quality of surface water, the monitoring network of which is insufficient. In this respect, this work aimed at a more systematic and comprehensive assessment of water quality in some rivers, tributaries of the river Vardar in Tikveš Basin, primarily based on heavy metals as the chemical parameters during 2010. Besides determining the distribution of heavy metals in the rivers, the secondary priority is given to identifying the natural and the anthropogenic sources of pollution. The assessment of water quality at small tributaries of the river Vardar in the Tikveš Basin in 2010, based on their pollution with heavy metals, can lead to a general conclusion that the Luda Mara River has the lowest summary quality at the measurement point downstream the urban settlement of Kavadarci. Exceeded concentrations of Mn, Cu and Cd were recorded in the water and of Cu and Ni in the sediment. The Blašnica River had high concentrations of arsenic in water whose origin is related to mining activities of the abandoned As-Sb-Tl mine of Allchar. Exceeded concentrations of Pb and Cu were also recorded in water as were concentrations of nickel and chromium in the sediment. The high values for Ni and Cr originate from mine activities of the Ržanovo mine (ferro-nickel ores), located in the very proximity of the river flow.**

Keywords- Rivers; Pollution; Heavy Metals; Water Quality; Tikveš Basin; Republic Of Macedonia

I. INTRODUCTION

Antagonism between intentions for accelerated development and limited available water resources accompanied with numerous water management problems in the territory of the Tikveš Basin, unavoidably leaves traces in water quality in general as the vital component of the environment [1]. For these reasons, a necessity of elaborate examination of all the factors of pollution and tendencies in the movement of quality of the water component in Tikveš imposes itself intuitively so that unwanted consequences are identified and prevented and measures for their future protection proposed. The subject of this work has involved water in smaller tributaries of the river Vardar within the Tikveš Basin, i.e. its state concerning pollution with some heavy metals as the criterion of quality. The goal of the work is to detect in a systematic manner the current quality, pollution and spatial distribution of heavy metals in the rivers concerned, and identify the natural and anthropogenic sources of pollution of the smaller rivers in the Tikveš Basin. The primary urge leading to the implementation of such a goal is the fact that in this respect, the scientific community has paid little attention to small rivers in the Tikveš Basin, which are not subject to adequate monitoring or where they are, it is done incidentally, and on the other hand, they are of huge importance in water supply, agriculture and energy provision for the population in the whole region. So far in the region, regular monitoring of the three largest rivers has been conducted with total four measurement stations included in the state-run River Monitoring System in Macedonia (RIMSYS), as in [2]. Those are the measurement stations on the Vardar (near the village of Nogaevci and Demir Kapija), the river of Bregalnica (near the village of Ubogo) and the river Crna (near the village of Palikura). The main assumptions of the existence of toxic metal pollution in the Tikveš rivers involve industrial plants, mining activities, polymetallic composition of minerals from the geological soil [3] and the increased concentration of some metals in the soils [4, 5].

II. STUDY AREA

Geographically, the Tikveš Basin covers areas in the central and the south parts of the Republic of Macedonia (Fig. 1). In spatial terms, the basin has a non-regular circular form and is located between 41005'30" - 41043'38" N and 21047' - 22019' E.

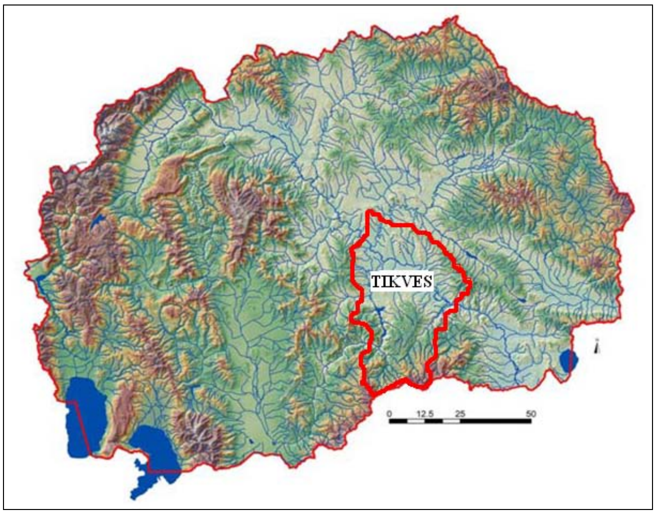

Fig. 1 Tikveš location in the Republic of Macedonia

The wavelike Tikveš Basin encompasses: the middle drainage basin area of the river Vardar, the lower parts of the drainage basin areas of the rivers Bregalnica and Crna River and the drainage area of the Bošava and the Luda Mara rivers on the whole (Fig. 2). In its natural boundaries, the Tikveš Basin covers 2060.54 km2, measured by the watershed line that accounts for 8% of the territory of the Republic of Macedonia. In territorial and administrative terms, Tikveš is divided in five municipalities with the population of 70,339 inhabiting 77 settlements, out of which three are regarded as urban settlements: Kavadarci, Negotino and Demir Kapija according to Census, 2002. The average population density is 32.8 inhabitants/km^2.

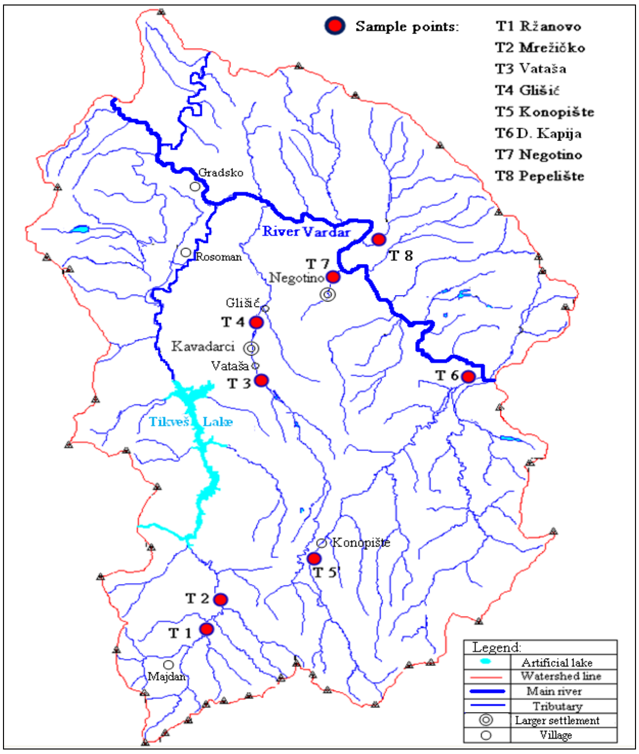

Fig. 2 The river network of the river Vardar in the Tikveš Basin and measurement points on some rivers where water monitoring was made

Tectonically, the Tikveš Basin has a graben structure that completely belongs to the Vardar zone [6].

The geological composition of Tikveš is a real mosaic of: igneous, metamorphic and sedimentary rocks of different age, from Precambrian to the youngest Holocene forms. According to the geological map [7], Paleogene sediments from the Upper Eocene flysch in the eastern part of Tikveš, and Neogene sand plates to the west from the river Vardar prevail in Tikves. Quaternary rocks are represented by volcanic and volcano-sedimentary rocks in the volcanic Kožuf-Vitačevo area covering approximately 300 km^2, in the form of effusive rocks of the andesite type and volcanogenic sedimentary forms as brechoid and fine-ground tuff, and andesite chocks. Climatically, the Tikveš Basin is considered one of the most arid areas in the Balkans.

The average water precipitation is less than 400 mm annually in the surroundings of the Municipality of Gradsko [8]. The climatic drought as the specific characteristic of the region is also reflected in its hydrological features. The rivers that are formed in the area of the Tikveš Basin and flow into the main recipient, the river Vardar, have total average yearly flow of 6 m^3/s, and their real specific outflow is 2.91 l/s/km^2, according to long-term measurements of Administration for Hydrometeorological Affairs from Skopje.

III. METHODS AND MATERIALS

A. Design

For the purpose of a denser network of measurement points that would reflect more objectively the condition with heavy metal pollution in rivers within the Tikveš Basin, several points on some streams in Tikveš were suitably selected for assessment of their quality during 2010. The selection of the measurement points was made deliberately, starting from objective indications that pointed indirectly or directly to certain anomalies in quality of the aquatic systems, which could negatively affect the main recipient in the region, the river Vardar, and thus the local population's health.

Spring/summer and autumn/winter test samples were submitted for analyses to two institutions: Institute for Public Health of the Republic of Macedonia, and the Laboratory of Atomic Spectroscopy within the Institute of Chemistry of the Faculty for Natural Sciences in Skopje. Except for the autumn/winter water samples, samples from the river sediments were also taken for the purpose of obtaining an insight into the possible contamination of the water systems in the past. Heavy metal concentration in the river sediment is expressed as mg/kg. The Republic of Macedonia has not adopted regulations on categorization of land concerning pollution with harmful matters, and therefore the existing Dutch standards are preferred in this paper [9].

B. Water Samples

Test water samples were taken from rivers in the area of the Tikveš Basin at different measurement points. The samples were taken in polyethylene containers previously cleaned with HNO3 (1+9), in compliance with ISO 5667-3(1). 100 ml homogenized sample was poured into a laboratory glass and dry-steamed after adding 1 ml HNO3 (65-67%). The mineralized residue after digestion was dissolved in 10 ml 4% (v/v) HNO3 and the solution thus obtained was then used for measuring by flame atomic absorption spectrometry (FAAS) and atomic emission spectrometry with inductively coupled plasma (ICP-AES). All the reagents and standard solutions used during the measurements had known analytical gradient. The basic standard solutions had mass concentration of 1000 mg/L (commercially available), out of which operational standards for the calibration curve were prepared.

For digestion of attic dust samples, open wet digestion with mixture of acids was applied. Precisely measured mass of dust samples (0.5 g) was placed in Teflon vessels and 5 ml concentrated nitric acid, HNO3 was being added, until the brown vapours came out from the vessels. Nitric acid is a very suitable oxidant for digestion of environmental samples. For total digestion of inorganic components 5-10 ml hydrofluoric acid was added. When the digest became a clear solution, 2 ml of HClO4 was added. Perchloric acid was used for total digestion of organic matter. After cooling the vessels for 15 min, 2 ml of HCl and 5 ml of H2O were added for total dissolving of metal ions. Finally, the vessels were cooled and digests quantitatively transferred to 50 ml calibrated flasks.

C. Reagents and Standards for ICP-AES

For this study reagents with analytical grade (or better) were used: nitric acid, trace pure (Merck, Germany), hydrofluoric acid, p.a. (Merck, Germany), perchloric acid, p.a. (Merck, Germany), hydrochloric acid, p.a. (Merck, Germany), and redistilled water was used for preparation of all solutions. Standard solutions of metals were prepared by dilution of 1000 mg l^{-1} solutions (11355-ICP multi Element Standard).

D. Instrumentation

The following elements were determined Al, As, Ba, Ca, Cd, Co, Cr, Cu, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn. Analyses were performed with atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian, 715ES). The optimal instrumentation and operating conditions for ICP-AES system are presented in Table 1.

The QC of ICP-AES determinations were performed by standard addition method, and it was found that the recovery for the investigated elements ranges between 97.5% and 100.8%. The same method was applied for the determination of some trace elements in the reference standard materials JSAC 0401 (soil) and SARM 3 (rock), yielding values very close to those certified.

TABLE I INSTRUMENTATION AND OPERATING CONDITIONS FOR ICP-AES SYSTEM

RF Generator					
Operating frequency	40.68 MHz free-running, air-cooled RF generator.				
Power output of RF generator	700–1700 W in 50 W increments				
Power output stability	Better than 0.1%				
Introduction Area					
Sample Nebulizer	V- groove				
Spray Chamber	Double-pass cyclone				
Peristaltic pump	0-50 rpm				
Plasma configuration	Radially viewed				
Spectrometer					
Optical Arrangement	Echelle optical design				
Polychromator	400 mm focal length				
Echelle grating	94.74 lines/mm				
Polychromator purge	0.5 L min^{-1}				
Megapixel CCD detector	1.12 million pixels				
Wavelength coverage	177 nm to 785 nm				
Conditions for program					
RFG Power	1.0 kW	Pump speed	25 rpm		
Plasma Ar flow rate	15 L min^{-1}	Stabilization time	30 s		
Auxiliary Ar flow rate	1.5 L min^{-1}	Rinse time	30 s		
Nebulizer Ar flow rate	0.75 L min^{-1}	Sample delay	30 s		
Background correction	Fitted	Number of replicates	3		
Element	**Wavelength, nm**	**Element**	**Wavelength, nm**	**Element**	**Wavelength, nm**
Al	396.152	Cu	324.754	Ni	231.604
As	188.980	Cr	267.716	Pb	220.353
B	249.678	Fe	238.204	Zn	213.857
Cd	226.502	Mn	257.610		

IV. RESULTS AND DISCUSSION

In order to assess the water quality of small tributaries of the river Vardar in the Tikveš Basin, which was the subject of the study in 2010, based on their pollution with some heavy metals, several water sample points were deliberately selected: Ržanovo and Mrežičko (river Blasnica), Vataša and Glišić (river Luda Mara), Konopište and Demir Kapija (river Bošava) and river Pepeliška and river Negotinska at its confluences (Fig. 2, Table 2). Also, the samples from river sediments were subjected to insight in 2010 at the same points, with the following results (Table 3).

TABLE II AVERAGE CONCENTRATIONS OF SOME METALS IN THE WATER OF SOME RIVERS IN THE TIKVEŠ BASIN IN 2010 (IN MG L-1)

Sample point	Al	As	B	Cu	Fe	Mn	Cd	Zn	Ni	Pb	Cr
The Blašnica (Ržanovo)	24.5	78.6	16.6	4.9	6.4	3.8	<0.01	25.7	5.0	33.0	<0.01
The Blašnica (Mrežičko)	10.6	39.8	28.4	11.1	16.6	1.4	<0.01	23.5	5.2	20.0	<0.01
The Luda Mara (Vataša)	174	10.2	11.8	5.0	135	3.8	3.0	3.0	5.1	7.0	<0.01
The Luda Mara (Glišić)	45.1	7.7	46.6	26.0	59.6	58.5	3.0	36.0	2.0	8.2	1.0
The Bošava (Konopište)	8.0	6.9	11.6	4.0	13.5	2.4	3.0	3.0	5.0	7.1	<0.01
The Bošava (D. Kapija)	20.0	8.6	22.4	5.0	7.4	2.3	5.0	6.0	1.0	0.01	<0.01
The Negotinska River	20.0	7.1	178	6.0	21.0	41.0	1.0	8.0	6.2	0.01	<0.01
The Pepeliška River	19.9	4.9	121	4.9	14.8	5.9	-	4.8	-	-	-

TABLE III AVERAGE CONTENTS OF SOME METALS IN THE SEDIMENT OF SOME RIVERS IN THE TIKVEŠ BASIN IN 2010 (IN MG/KG)

Sample point	Al	Cu	Fe	Mn	Zn	Ni	Pb	Cr
The Blašnica (Ržanovo)	34372	19.2	29291	585	46.7	406	28.0	349
The Blašnica (Mrežičko)	27719	17.5	23147	405	39.1	297	27.2	228
The Luda Mara (Vataša)	29270	14.6	18591	340	43.3	28.0	9.6	37.9
The Luda Mara (Glišić)	31571	37.6	20538	386	109	62.7	28.7	53
The Bošava (Konopište)	30777	14.4	21681	366	51.4	23.2	57.5	27.2
The Bošava (D. Kapija)	40987	31.6	32363	580	109	109	18.7	176
The Pepeliška River	33629	28.4	28470	617	44	140	8.9	135

The Blašnica River was the subject of testing at two intentionally selected sample points. The selection of the river and the measurement points was initiated since there was a justified risk for the environment from the past and the current activities in the Ržanovo mine (ferro-nickel ore) [4, 10] and Alšar mine (arsenic-antimony-thallium ore) [3, 5, 11, 12], located in its drainage basin area, and its confluence into one of the largest artificial lakes in the Republic of Macedonia, Tikveš Lake, a potential donor of drinking water in the region [13]. Amongst the group of toxic metals subject to testing during 2010 in the River Blašnica water, at the sample points near Ržanovo (41^{o}11´19,66" **N**; 21^{o}58´10,11" **E**; Hs 610 m) and Mreži~ko (41^{o}12´34,05" **N**; 21^{o}59´09,34" **E**; Hs 474 m), it was found that their concentration was mainly within the limits for the corresponding class I-II (Al, B, Fe, Ni, Mn and Zn), according to the national Regulations on Classification and Categorisation of Rivers [14].

Considerably lower water quality was observed with regard to the contents of arsenic, lead and copper. The arsenic concentration at the Ržanovo sample point (T1, Fig. 2), which was 5 kilometres downstream the abandoned Alšar mine, rich in arsenic and antimony ores, corresponded in average to the class V with 78 µg/l (Table 2, Fig. 3).

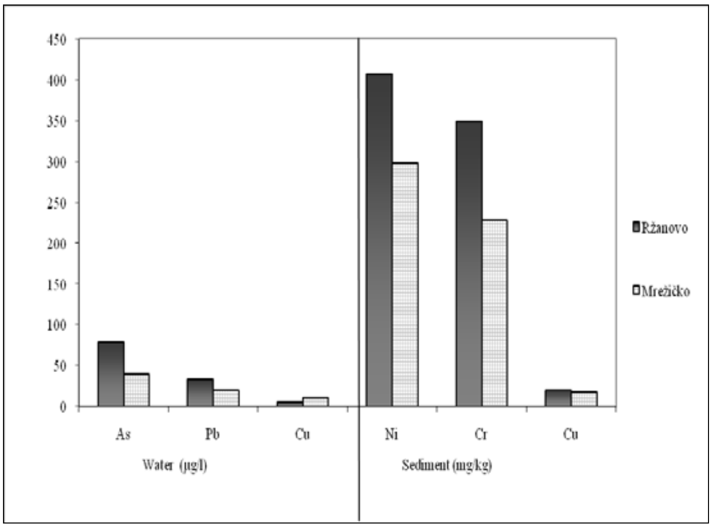

Fig. 3 Distribution of some critically prevalent metals in the water and the sediment along the flow of the river Blašnica at the sample points: Ržanovo (T1, Fig 2) and Mrežičko (T2, Fig 2) in 2010

At the downstream sample point near the village of Mrežičko (T2, Fig. 2), the arsenic concentration decreased to 39 µg/l, the level that corresponded to the III-IV class (Table 2, Fig. 3). The situation with the presence of copper in the Blašnica River was opposite in that going downstream, its concentration increased and at the measurement point near

Mrežičko (T2, Fig. 2), it reached the level of the III-IV class with the concentration of 11 µg/l (Table 2, Fig. 3). Copper is naturally at the 25th place according to the prevalence of elements in the lithosphere [15], and a possibility for its natural prevalence in the basin of the River Blašnica is very likely. Increased concentrations of lead in the Blašnica River measured at the upper sample point near Ržanovo (33 µg/l, class III-IV) were probably the result of mining waste since its most recognized sources into the environment: industrial lead waste, leaded petrol, military industry products, metallic product dyeing agents, production of batteries, etc. [16] were not present in the catchment area of the Blašnica River.

Its concentration downstream was decreasing within the limits below the maximum allowed concentration (MAC) for the highest class of quality of the rivers (Table 2, Fig. 3).

Contrary to initial expectations for the increased pollution of the river with nickel and iron due to the evident flow of mine waste from the nickel-iron mine of Ržanovo [4, 10] into the riverbed, the results corresponding to the class I-II were surprising. But the assumptions of risk from contamination of the Blašnica River with those toxic metals were confirmed by chemical analysis results for the sediment taken at the same sample points Ržanovo (T1, Fig. 2) and Mrežičko (T2, Fig. 2). They demonstrated retroactive precipitation of nickel and chromium as toxic metals in the sediment of the river (Table 2, Fig. 1). Increased presence of these heavy metals in the water and the sediment of the Blašnica River at the two sample points during 2010 undoubtedly reflected the influence of mining activities in its catchment area, which led to their enrichment with arsenic and nickel. Naturally, the flow of the Blašnica is contaminated with chromium and copper from the minerals existing in the surrounding rocks and soil, which is considered an area with polymetallic deposits with volcanic rocks originating from the young Pleistocene, within the wider catchment area [3]. Decreasing concentrations of two heavy metals respectively, i.e. nickel and chromium in the sediment and arsenic and lead in the water downstream the Blašnica River and as one distanced from the mines: the mines Alšar and Ržanovo, the influence of which was not questionable in this case, could be stated. Ultimately, we cannot exclude the point that globally, arsenic is the most common element in rivers along young mountains [17], as is the case with the Blasnica whose flow stretches along mountains with expressed young volcanism [10]. The presence of arsenic in waters from Kužuf Mountain was known from our previous results [18].

Comparison of the samples taken from the Vataša River (The Luda Mara) at the sample points: Vataša, T3, Fig. 2 (41°24´17,52" **N;** 22°01´30,67" **E**; Hs 330 m), before entering into the city area, and the village of Glišić, T4, Fig. 2 (41°27´19,47" **N**; 22°01´17,64" **E**; Hs 221 m), downstream of the town of Kavadarci, generally highlighted the negative anthropogenic influence of the town of Kavadarci the waste water of which was discharged untreated in the river. Concentrations of heavy metals in the Luda Mara River increased downstream the urban area as a result of many industrial facilities, the waste outlets of which ended into the Luda Mara most commonly without any waste water purification treatment.

The manganese (58.5 µg/l) and the copper (26 µg/l) concentrations, which were considerably increased downstream from the town of Kavadarci, at the lower sample point near the village of Glisic (T4, Fig. 2) and corresponded to the III-IV class, reflected most adequately such a state (Table 2, Fig. 4). The value for cadmium (3.0 µg/l), which corresponded to the III-IV class was unaltered at the two measurement points, before and after the exit from the city area, and indicated its natural presence from dissolved minerals in the soil, not expressing any anthropogenic involvement as a possible source of its emission in the river (Table 2, Fig. 4).

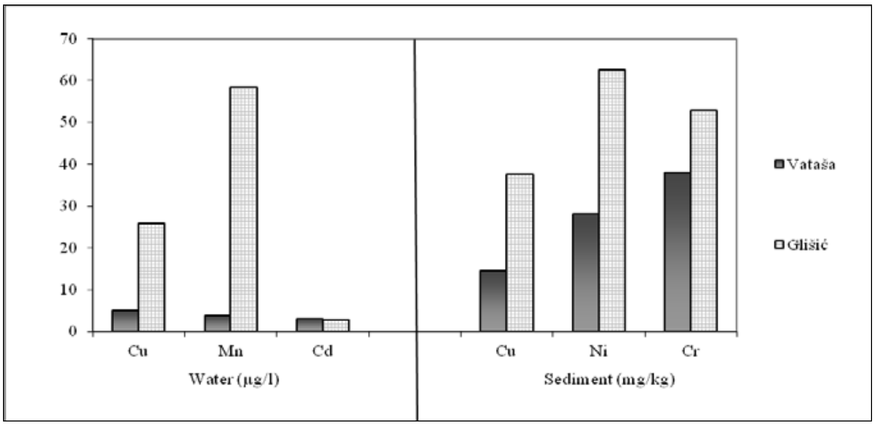

Fig. 4 Distribution of some critically prevalent metals in the water and the sediment along the flow of the Luda Mara River at the sample points: Vataša (T3, Map 2) and Glišić (T4, Map 2) in 2010

Except in water, samples from the sediment also demonstrated permanent retrospective precipitation of nickel and copper that had contaminated the Luda Mara River for a long period downstream the town of Kavadarci, and that was likely a consequence of metal processing facilities located next to the river bed (Table 3, Fig. 4). The same happened with the values of other metals in the sediment that were considerably increased at the lower measurement point near the village of Glišić (T4, Fig. 2). The exceeded reference value for the properness of the soil, that of the copper in the sediment of the Vataška River near the village of Glišić (T4, Fig. 2) indicated that, regardless of its low concentration in the water, retrospectively, it had been anomalously present on a long-term basis and had sorbed over the sediments as shown by analyses (Table 3, Fig. 4). Increased presence of nickel in the sediment indicated retroactive contamination of the river with the toxic metal, which had most probably derived from industrial sources due to its absence at the measurement point upstream the settlement of Kavadarci.

As for the Bošava River the water of which was collected at the spring for water supply of the urban populations in the Tikveš Basin and irrigation of agricultural areas, determination of the presence of some heavy metals was made at two measurement points: Konopište T5, Fig. 2 ($41^o14^{'}35,37''$ **N**; $22^o04^{'}32,10''$ **E**; Hs 674 m) in the upper part of the drainage basin, and Demir Kapija T6, Map 2 ($41^o24^{'}22,83''$ **N**; $22^o14^{'}50,85''$ **E**; Hs 104 m), before its confluence into the Vardar River. Although the drainage basin of the Bošava River was sparsely populated and did not have any major industrial capacities, general estimation that could be derived from the performed analyses was that heavy metals in water downstream the river tended to increase but the advantage regarding the river eco-system was that it evolved within the anticipated concentrations for the Class I-II quality (Table 2). Anomalous values above MAC for the I-II class were only determined for cadmium, which was found in concentrations for the III-IV class at the two sample points, with a tendency to increase downstream from Konopište T5, Map 2 (3.0 μg/l) towards the confluence nearby Demir Kapija T6, Map 2 (5.0 μg/l) of the Bošava River (Table 2, Fig. 5). Due to the absence of industrial facilities and the presence of cadmium in the upper, mountain part of the catchment area that was under environmental protection, we were of opinion that its origin in the Bošava River was natural and derived from dissolved minerals in the rocks within the geological composition. The same estimation could be given from the results of the sediment, which obviously showed that at the lower sample point outside Demir Kapija (T6, Fig. 2), there had been permanent precipitation of nickel and chromium, the levels of which were increased anomalously (Table 3, Fig. 6). A similar situation was also recorded near the Blašnica River, and the common characteristic connecting the two rivers was their origins in an area under volcanic cones of Paleo-volcanic relief with volcanic rocks of polymetallic composition.

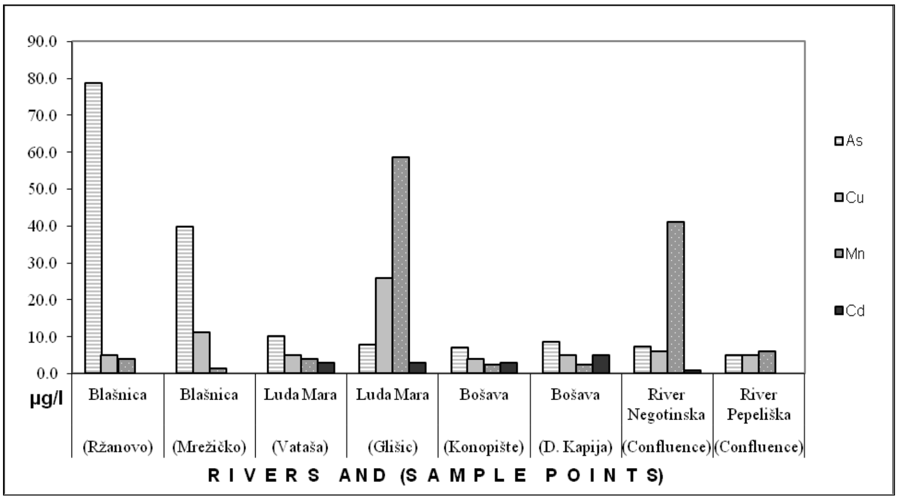

Fig. 5 Average values of the critically prevalent metals in the water of some rivers in the Tikveš Basin in 2010

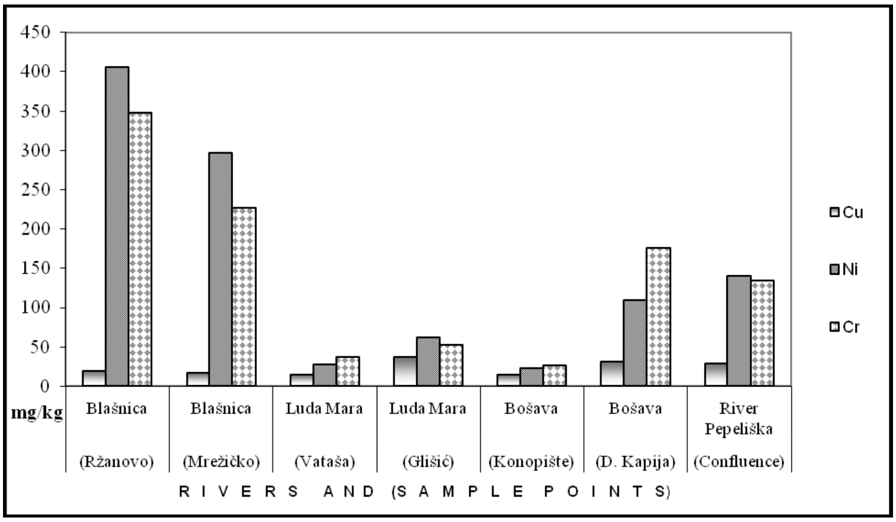

Fig. 6 Average values of the critically prevalent metals in the sediment of some rivers in the Tikveš Basin in 2010

The Negotinska River was the main recipient of households and industry waste water in the town of Negotino, with an anthropogenic load of approximately 15,000 inhabitants in the catchment area. The subject of the testing was only quality of its water with regard to the presence of heavy metals downstream Negotino T7, Fig. 2 ($41^o29'51,56''$ **N**; $22^o06'06,53''$ **E**; Hs 119 m), with a purpose of assessing the anthropogenic load of the town over the river. A special symptomatic feature that initiated concern and the research activity was the paradoxical hydrological regime. Actually, the river characterized with small flow and was of a periodical nature in the upper stream, before flowing into the populated settlement Negotino, whereas downstream, the flow was of a permanent nature and had perceivably increased flow, which most likely originated from the town waste water. It was a sufficient indication of deterioration of water quality, which was the subject of evaluation before the confluence into the Vardar River (T7, Fig. 2).

Chemical analysis of samples for the presence of heavy metals in the Negotinska River showed surprising results, having in mind that all the waste water from the city area was discharged into the river untreated. So, concentrations of majority of metals in the water ranged within low limits adequate for the I-II quality class, except for cadmium (1.0 µg/l), the level of which corresponded to the III-IV class (Table 2, Fig. 6). Still, this was not sufficient to attribute an anthropogenic pressure on the river if one took into account that all the right tributaries into the Vardar River, which originated in the volcanic Kožuf-Vitačevo area in the Tikveš Basin [10], had increased cadmium concentration in water (Table 2, Fig. 6).

Unlike the right tributaries of the Vardar River, the left ones in the Tikveš Basin flow through arid, bared flysch sediments from the Eocene and are characterized with a torrential property. Their catchment areas are almost completely depopulated with no influential industrial capacities as a potential source of contamination. In this respect, the purpose was to estimate, above all, the natural forms of contamination of the Pepeliška River as a left tributary, and find some comparable base with the rivers that flew into the Vardar from the right. From water samples taken in 2010 and analysis of heavy metal concentrations, preliminary hypotheses that it was about a river with high water quality, mainly in the I-II class at T8 (Fig. 2) were immediately proved (Table 2, Fig. 6). A real breakthrough ensued with the results from the sediment where concentrations of nickel and chromium were increased anomalously, for which there were reasonable assumptions that they had been naturally dissolved from minerals of the soil and then deposited over the river sediment (Table 2, Fig. 4). This finally shaped the mosaic of one of the general conclusions in this paper that certain heavy metals (Cr, Ni, Cd) in the water and in the sediment that are above referent values according to the Dutch standards [9] occurred in all the tributaries of the Vardar River in the Tikveš Basin and were of the natural origin. Confirmed concentrations of nickel in the rocks of the lithosphere that can naturally contain from 2 ppm (sandy sediments) to 200 ppm in basalts speak in favour of such a conclusion [15]. With serpentinite, it can reach concentration of up to 500 ppm [19]. All these rock types, which contain considerable contents of nickel, are very prevalent in the Tikves region, according to the geological map. Moreover, some previous examination of soil has pointed to critically high concentrations [9] of nickel and chromium in the Eocene flysch, which is widely prevalent in the Tikveš Basin [4].

Comparison of the results of sediment testing in the right tributaries of the Vardar in the region, undoubtedly leads to a conclusion that with almost all of them there is increased prevalence of those metals (chromium, nickel). On the other hand, the Pepeliška River is not disposed on the volcanic area of Kožuf-Vitačevo, however, as in Serta Mountain [6], where its spring area is located, was affected with young volcanism in late Neogene and early Pleistocene. Finding chronological coincidence with similar geotectonic processes and the geological composition of the soil, on which the Tikveš tributaries into the river Vardar are disposed nowadays, is complemented with coincidence in the composition of some heavy metals in their sediments, in particular nickel and chromium. If the human factor is only partially excluded, concerning demographic depopulation in the catchment areas of some rivers, one can very likely conclude that those toxic metals in water or the sediment derive from natural dissolution of minerals from the basis.

In general, the higher content of these elements (Ni, Cr, and Cd) in the investigated samples is closely dependent on the lithogenesis of the Tikveš region [4, 5]. Their highest contents were found in areas of Paleozoic and Mesozoic rocks and Eocene upper flysch zone and their lowest values in area of the Pleistocene tuff, Holocene deluvium and Holocene alluvium of the rivers Luda Mara, Crna Reka and Vardar [4, 5].

Several measures should be taken in order to reduce the impact of the mining activities including the regulation of mining waste disposal. In the urban area it is necessary to introduce waste treatment plants for municipal wastewaters in the larger settlements (the cities Kavadarci, Negotino and Demir Kapija).

V. CONCLUSION

The assessment of water quality at small tributaries of the river Vardar in the Tikveš Basin in 2010, based on their pollution with heavy metals, can lead to a general conclusion that the Luda Mara River has the lowest summary quality at the measurement point near Glišić (T4, Fig. 2) downstream the urban settlement of Kavadarci. Exceeded concentrations of: Mn, Cu and Cd were recorded in the water, and of Cu and Ni in the sediment. The least loaded with heavy metals is the Bošava River at the upper sample point near the village of Konopište (T5, Fig. 2) where an increasing level of Cd was only recorded in water, and it was of natural origin. The Blašnica River had high concentrations of arsenic in water at two sample points (T1 and T2, Fig. 2), and its origin was related to mining activities of the abandoned mine of Alšar (arsenic-antimony-thallium ore), so that its concentrations downstream showed mild decline. Exceeded concentrations of lead and copper were also recorded in water as were concentrations of nickel and chromium in the sediment. The high values for Ni and Cr originate from mine activities of the Ržanovo mine (ferro-nickel ores), located in the very proximity of the river flow. Concentrations above MAC were also detected in the Negotinska River before the flow, with regard to Cd, and in the sediment of the Pepeliška River with regard to Ni and Cr.

Anthropogenic sources include the urban, rural and industrial waste water that is dumped untreated into: the Luda Mara, the Blašnica and the Negotinska River. The most intensive pressure is exerted by metal industrial facilities in the town of Kavadarci, which load the Luda Mara River downstream with manganese, copper and cadmium. The Ržanovo mine obviously contaminates the river Blašnica with Ni, and the alarming ceiling levels along the flow belong to arsenic as the consequence of the abandoned Alšar mine in its upper flow.

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