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MONITORING OF POLLUTION WITH HEAVY METALS AND THEIR INFLUENCE IN AGRICULTURAL PURPOSES OF CERTAIN TRIBUTARIES OF VARDAR RIVER IN SKOPJE VALLEY, REPUBLIC OF MACEDONIA

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ABSTRACT

Skopje Valley is one of the largest and most populous regions in the country. Waste water from households, industry and agriculture end up in the Vardar River as the largest drainage artery in the region and beyond. However in the section of Skopje, the Vardar River receives several tributaries of which two are international waterways. The quality of the tributaries of Vardar River in Skopje Valley, are not subjected to regular monitoring, and the same are used for irrigation or are recipients of wastewater from the local population and industry. The waters of the tributaries of Vardar River string Skopje section according to the legal regulations of the Republic of Macedonia, show solid summative quality in terms of the burden of heavy metals. Annual regime of heavy metals refer increased concentrations which leadsto reduced water quality. What is more concerning is the amount of burden, manganese, cadmium, iron and copper in some tributaries in certain periods that reduce irrigation eligibility for agricultural purposes.

Keywords: Skopje Valley, tributaries, measuring point, pollution, heavy metals, etc.

INTRODUCTION

Vardar River Basin covers 80% of the territory of the Republic of Macedonia. It is also the largest recipient of industrial waste waters, as well as the largest contributor of water for irrigation of all possible runoff in the country. Numerous natural and anthropogenic factors undoubtedly change the water quality of the Vardar River in Skopje Valley. On the other hand, the Vardar River in Skopje Valley receives six tributaries with a constant flow (longer than 10

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km) whose quality is not subjected to regular monitoring by the merits institutions. For these reasons, spontaneously occurred the need for systematic assessment of water quality in some tributaries of Vardar River in Skopje Valley in terms of heavy metal contamination as a criterion for quality. Heavy metals are among the most common environmental pollutants and their occurrence in water and biota indicates presence of natural or anthropogenic sources [1]. In this paper were studied the waters of the tributaries of the Vardar River in Skopje Valley, which were monitored usually before their confluence as follows: Lepenec, Pchinja and Markova River. The assessment of the water quality was based on 8 heavy metals as a criterion for quality. The main goals of the paper is to detect their level of contamination as well as the impact on the recipient, especially if we know that some of the tributaries are international rivers and bring water from neighboring regions such as Lepenec (which originates in the Republic of Kosovo) and Pcinja (which rises in the Republic of Serbia). The secondary objective of the research is to assess their value in use for irrigation, and to identify natural and anthropogenic sources of pollution in order to propose the most appropriate measures to prevent pollution and improve the quality of water of the tributaries of Vardar in Skopje Valley.

STUDY AREA

Skopje Valley is situated in the northern part of the Republic Macedonia. It occupies the high basin of the Vardar River territory bounded by the mountains Goleshnica, Karadjica, Suva Planina, Suva Gora, Zeden, Skopska Crna Gora and the Mountain Gradishtanska [2]. Skopje Valley covers also the lower catchment areas of major tributaries (Treska, Lepenec, Pchinja) and plum with some smaller tributariesin (Serava, Markova Reka). In this framework the Skopje Valley occupies 1924.2 km^2 or 7.5% of the territory of the Republic of Macedonia, the flat strip is up to 300 meters above sea level accounted for 343.9 km^2 (fig. 1).

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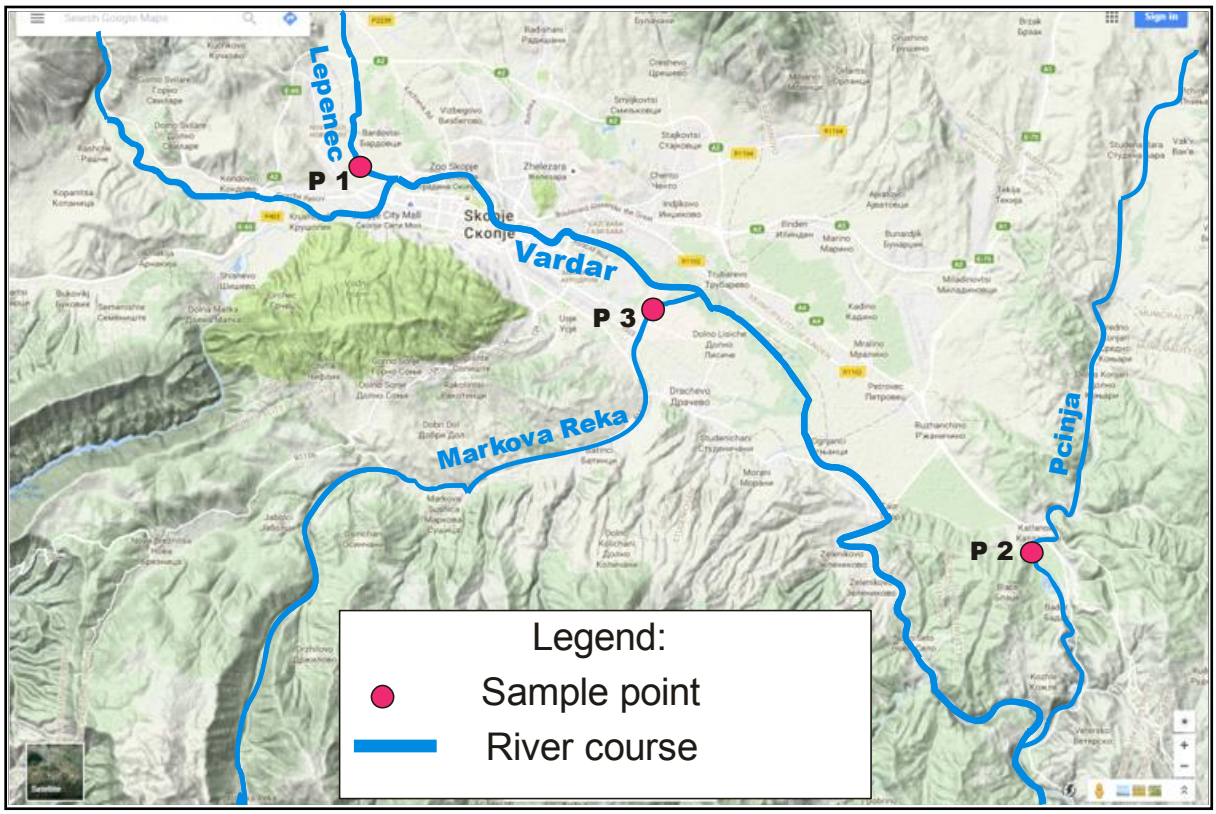

Figure 1. The drainage basin of Vardar River and its tributaries through the Skopje Valley

METHODS AND MATERIALS

With the intention to objectively detect the pollution of the waters of the tributaries of the Vardar River in Skopje Valley, over the 11 months of 2009/2010 were purposefully selected three points on rivers (tributaries) to assess the quality through the monitoring of samples which were analyzed monthly. The choice of measurement points was deliberately chosen, regarding practical reasons. Monitoring section of the Lepenec River as left tributary of Vardar was selected before the confluence, in order to assess the impact on the recipient by the neighboring regions (Republic of Kosovo) where the stream comes from (point 1, fig. 1). Pcinja River, which drains water from neighboring Serbia and Kumanovo Valley (in Macedonia) was followed at the entrance to Skopje Valley in Katlanovo, because its confluence is located outside (downstream) from Skopje Valley as studied area (point 2, fig . 1). The only right tributary, the Markova River was monitored before it joins Vardar River (point 3, fig. 1). Water samples were collected in polyetilene bottles previously washed with hydrochloric acid and rinsed out with abundant-distilled water in the laboratory and with abundant river water before collection. The heavy

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metals as parameters were analyzed in the laboratory of the Hydrometeorological Service. Heavy metals concentration of Fe, Mn, Pb, Cd, Zn, Cr, Ni, and Cu were determined by atomic absorption spectrometry using Varian 220 by graphite furnace and flame technique. As methods for determination of these parameters were used methods recommended by Standard Methods for the Examination of Water and Wastewater APHA, EPA, and EN/ISO methods. Water quality assessment was based on Macedonian regulation for classification of water quality [3]. According to the Macedonian regulation water is classified in five classes, from very good (class 1) to very bad (class 5). The results are statistically processed, and cartographic representation of the test area as a three-dimensional animation is used by software Earth Explorer, modified by package Surfer 8th.

RESULTS AND DISCUSSION

Regarding the burden of Vardar River water with heavy metals, subject for review were the: iron, manganese, lead, zinc, chromium, cadmium, nickel and copper. These substances are considered toxic in relatively low concentrations to plant and animal life and tend to accumulate in the food chain.

Table 1. Concentrations of heavy metals in the water of the Lepenec River (expressed in µg/l)*

Period	PARAMETERS							
	Fe	Mn	Pb	Zn	Cd	Cr	Ni	Cu
sep./2009	14,00	68,00	3,10	3,00	0,13	0,27	0,56	1,16
okt./2009	84,00	22,00	1,20	30,00	0,06	0,74	1,64	4,72
nov./2009	190,00	7,00	2,10	0,20	0,20	0,70	0,86	0,56
dec./2009	129,00	47,00	3,10	100,00	3,20	1,80	1,49	5,64
jan./2010	80,00	52,00	1,40	62,00	0,14	0,54	3,40	3,35
feb./2010	196,00	24,00	1,00	71,00	0,41	1,50	2,30	1,46
mar./2010	68,00	9,00	0,70	56,00	0,52	0,64	2,38	2,53
apr./2010	68,00	9,00	0,40	5,60	1,56	0,71	1,80	7,74
may/2010	80,00	6,00	3,90	22,00	0,22	0,93	1,95	0,05
jun./2010	93,00	24,00	1,30	34,00	0,05	1,39	0,89	3,82
jul./2010	101,00	13,00	0,20	40,00	0,07	1,19	2,05	1,94
Σ (average)	**100,27**	**25,55**	**1,67**	**38,53**	**0,60**	**0,95**	**1,76**	**3,00**

* yellow highlighted concentrations are equal to quality of class III-IV

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Table 2. Concentrations of heavy metals in the water of the Pcinja River (expressed in µg/l)*

Period	PARAMETERS							
	Fe	Mn	Pb	Zn	Cd	Cr	Ni	Cu
sep./2009	18,00	36,00	3,51	2,00	0,00	0,73	1,24	1,34
okt./2009	271,00	23,00	1,77	2,00	0,00	0,49	9,27	4,73
nov./2009	91,00	28,00	1,83	0,20	0,10	0,10	0,31	0,16
dec./2009	221,00	23,00	1,28	77,00	0,22	1,55	1,60	5,01
jan./2010	92,00	22,00	1,66	41,00	0,04	0,18	1,95	2,81
feb./2010	1191,00	28,00	4,53	35,00	0,17	1,10	0,89	5,53
mar./2010	369,00	28,00	1,65	33,00	0,07	0,08	2,71	5,05
apr./2010	369,00	28,00	3,46	33,00	0,62	0,26	0,51	11,14
may/2010	58,00	7,00	2,42	30,00	0,05	0,43	1,64	4,56
jun./2010	195,00	5,00	0,25	38,00	0,06	0,57	0,55	3,21
jul./2010	91,00	11,00	2,94	37,00	0,07	1,28	6,01	0,56
Σ (average)	**269,64**	**21,73**	**2,30**	**29,84**	**0,13**	**0,62**	**2,43**	**4,01**

* red highlighted concentrations are equal to quality of class V

Table 3. Concentrations of heavy metals in the water of Markova River (expressed in µg/l)*

Period	PARAMETERS							
	Fe	Mn	Pb	Zn	Cd	Cr	Ni	Cu
sep./2009	26,00	59,00	3,79	4,00	0,03	0,78	0,18	2,09
okt./2009	241,00	37,00	1,79	0,00	1,55	0,57	2,78	16,05
nov./2009	26,00	43,00	2,02	0,20	0,25	0,11	1,07	0,06
dec./2009	117,00	53,00	2,92	79,00	2,92	0,75	1,53	5,86
jan./2010	81,00	54,00	1,67	80,00	0,07	0,32	3,40	3,53
feb./2010	279,00	22,00	1,91	60,00	0,12	1,34	1,36	5,35
mar./2010	213,00	22,00	1,60	33,00	0,23	0,16	2,02	4,18
apr./2010	213,00	22,00	0,88	33,00	0,17	0,38	0,66	2,58
may/2010	65,00	8,00	0,64	43,00	0,12	0,65	0,49	5,79
jun./2010	110,00	2,00	0,32	61,00	0,33	0,32	0,55	2,58

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jul./2010	46,00	23,00	2,65	47,00	0,02	0,80	6,66	0,56
Σ (average)	**128,82**	**31,36**	**1,84**	**40,02**	**0,53**	**0,56**	**1,88**	**4,42**

∗ yellow highlighted concentrations are equal to quality of class III-IV

Figure 2. Annual regime of the concentration of heavy metals in the waters of the Lepenec River (µg/l)

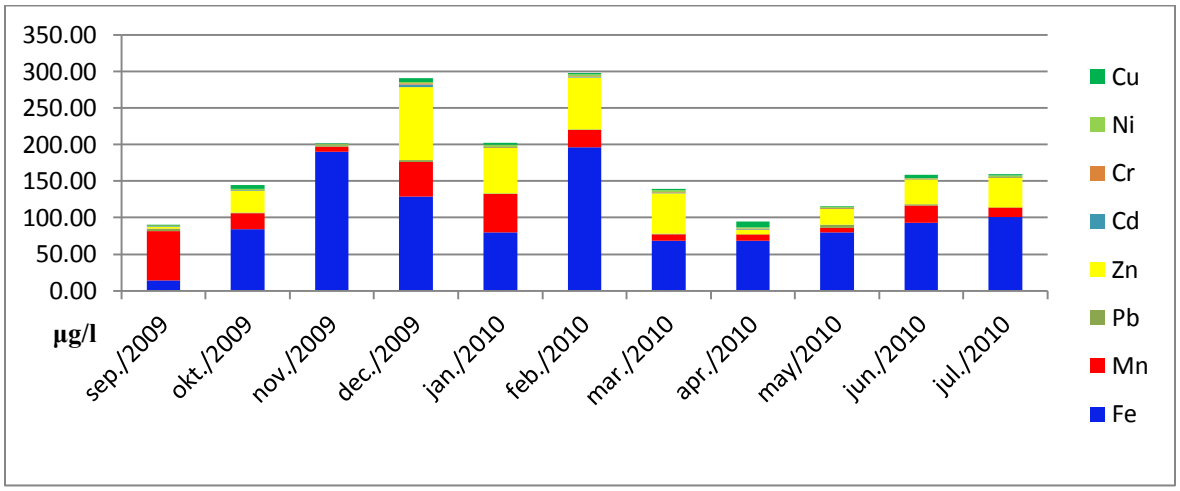

Figure 3. Annual regime of the concentration of heavy metals in the water of the Pcinja River (µg/l)

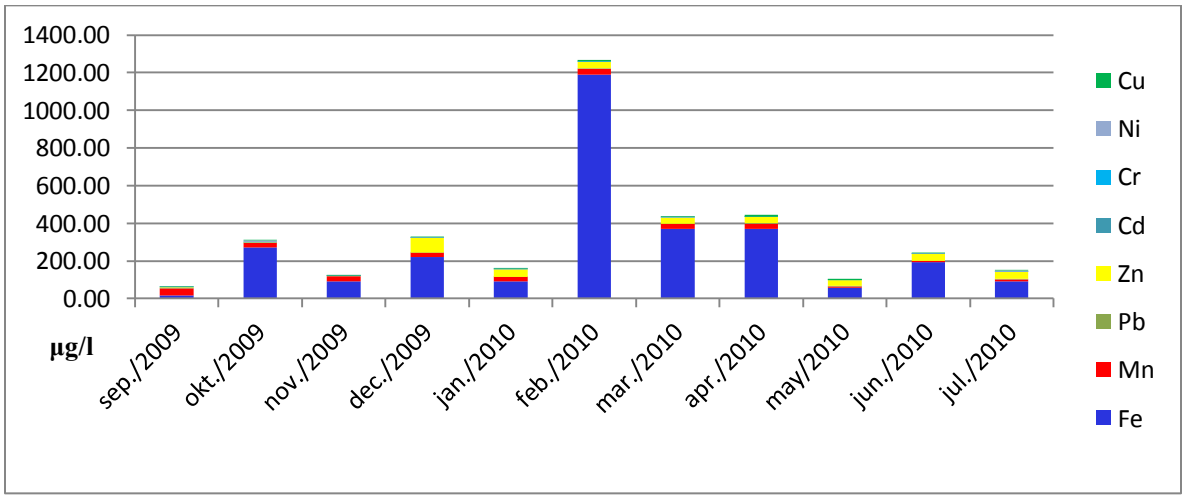

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Figure 4. Annual regime of the concentration of heavy metals in the water of Markova River (µg/l)

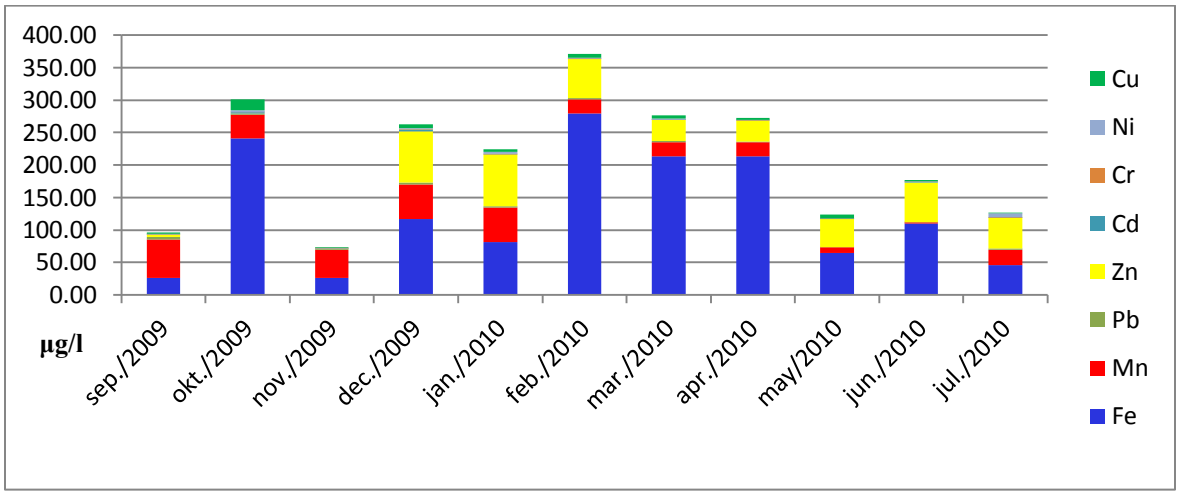
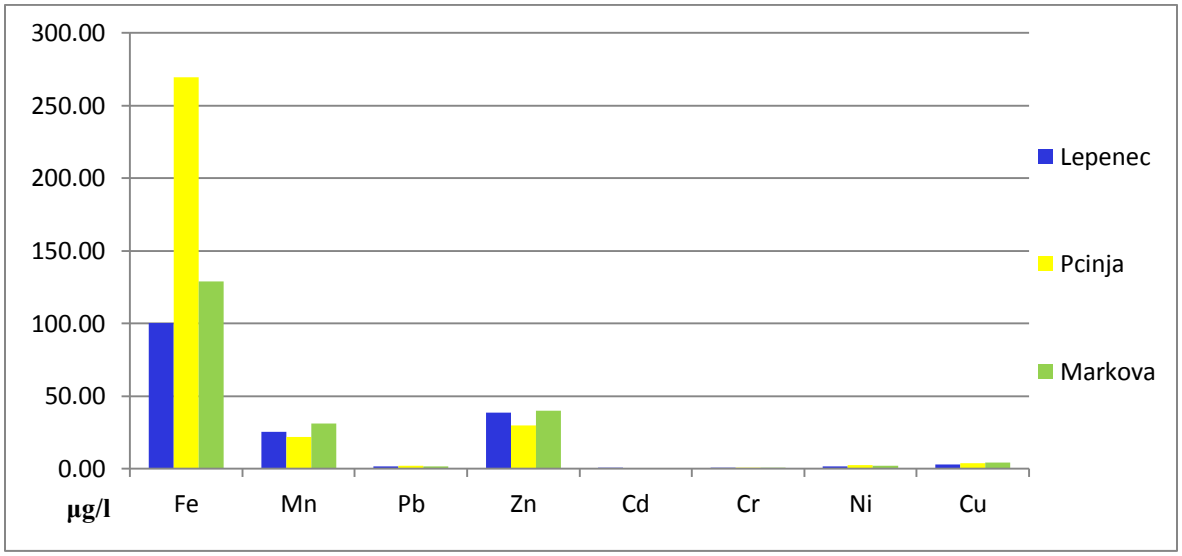


Figure 5. Annual regime of the concentration of heavy metals in the water of the rivers Lepenec, Serava, Pcinja and Markova (expressed in µg/l)



Lepenec River rises in the Republic of Kosovo. The total length of the watercourse is 75 km. The catchment area covers 770 km^2. In the Vardar River it flows from the left side at an altitude of 253 meters. Samples of its waters were sampled before it joins Vardar River (point 1, fig. 1). Regarding the Regulation on classification of rivers in Republic of Macedonia, the annual concentrations of the season (2009/2010) of heavy metals tested expressed relatively good

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quality and mostly concern within quality class I-II. Abnormalities appear only in terms of manganese in incidental cases when values exceed the quality class III-IV. Also, there was some exceeding in the maximum allowable concentrations of cadmium which correspond to quality class III-IV (tab. 1, fig. 2, 5). Manganese in the water is naturally derived mostly from dissolution of shale and sandstone, and we consume it through metallurgical activities [4,5], whose elevated levels likely originated from Kosovo. Manganese reduces the photosynthesis in plants by reducing the absorption of sunlight. In the irrigation water it must not exceed a concentration of 0,2 μg/l [6], which apparently is exceeded enough. Cadmium is a toxic metal that is very rare in the nature. In some rivers in R. Macedonia is naturally present in certain Paleozoic and Mesozoic rocks [7]. The human factor introduces cadmium into the waters by cement dust, then from smelting zinc ore, production of batteries and other [7, 8]. In irrigation water it must not exceed 0,01 μg/l in long terms, because it performs a reduction in the plant growth and changes in cell metabolism by reduced chlorophyll [9] reflecting the reduced value of irrigation in the river Lepenec on the territory of the Republic of Macedonia. The presence of cadmium in the river Lepenec in Skopje Valley may be due to the industrial impact (cement industry, etc.) originating from Kosovo. In terms of the need for irrigation, in the other heavy metals the concentrations on long terms showed some anomalous values, except lead (average 2,3 μg/l, tab. 1) where it is allowed up to 5,0 μg/l [10].

Pcinja River rises in Serbia. The length of the watercourse is 129 km and the total catchment area is 3,140 km^2. In the Vardar River flows from the left side at an altitude of 191 meters downstream from Skopje Valley so that samples of the water flow were examined from the entrance to Skopje Valley nearby the village of Katlanovo (point 2, fig. 1). A review of the results indicates periodic tendency of slight increase in the concentrations of cadmium and copper in occasional boundaries to quality Class III-IV, which is expected to watercourse which drains a large area. Copper as a heavy metal in aquatic ecosystems derived from certain minerals (limestone, sandstone), mining and metallurgical activities and excessive use of fungicides in agriculture [11]. In the irrigation water it must not exceed a concentration of 0,1 μg/l. In the Pcinja River in Skopje Valley once its concentration was increased to a level of class III-IV (11,14 μg/l), which emphasizes the anthropogenic impact, although the average values correspond to quality class I-II (tab. 2, fig. 3, 5). Lowest water quality in the examined period in Pcinja River was observed in terms of iron, which in February was recorded sample concentration appropriate for class V (1191 μg/l), and in the following months: March and April up to class III- IV (tab. 2, fig. 3, 5). The increased concentration of iron in the water is upsetting the osmoregulation of the plants, and thus the quality of agricultural food. In the irrigation water it is not recommended to be up to concentrations above 5 μg/l [6]. Analyzes carried out in this regard show that irrigational potential of the water flow in Katlanovo (point 2, fig. 1) is minimized based on annual regime of iron and other seven metals which were tested with most

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allowed presence up to 0.1-0.2 µg/l (chromium, copper, manganese). This situation is particularly alarming considering that in the basin of Pcinja River intensively cultivated plants with high absorbing power of heavy metals from water and soil. Like for example, onions and garlic [12].

Markova Reka (River) is a tributary of the Vardar River which rises in the massif Jakupica at 1900 meters and flows into the Vardar River nearby Dračevo at an altitude of 212 meters. The length of the watercourse is 30 km. Samples of the water flow were examined before it joins Vardar River (point 3, fig. 1). The significance of the water quality or mode of heavy metals in the water flow is seen in the fact that its resources are used for irrigation of agricultural land in three villages in the basin, but also for exploitation of quartz sand from the riverbed. Some anomalies (tab. 3, fig. 4, 5) were registered in terms of the cadmium (very often), manganese (occasional occurrence) and copper (incidental occurrence). Frequent, but slightly exceeding the maximum allowable concentrations of cadmium (class III-IV) may be due to natural erosion processes, but also from the cement dust that comes from immediate excavation of marls and from the cement processing. The presence of sands in the basin which easily dissolve and anthropogenic activities (industry and the use of fungicides) are potential sources of manganese and copper that at the bottom of this mountainous stream burden manganese and copper to levels appropriate for class III-IV (tab . 3, fig. 4, 5). In terms of maximum allowable concentrations of lead in long terms, from the surveyed heavy metals, the water's just show correctness regarding the lead with an average annual concentration of 1,84 µg/l (tab. 3), which is allowed up to 5.0 µg/l.

CONCLUSION

In this paper were studied the waters of the three tributaries of the Vardar River in Skopje Valley, one of which with a local catchment area (Markova Reka) and two international waterways (rivers Lepenec and Pchinja) whose water resources are used for irrigation. The assessment of the water quality of threer streams was based on 8 heavy metals as a criterion for quality that has a significant impact on agricultural production in case of usage for irrigation. According to the limit values for categorization of watercourses established in the Republic of Macedonia was detected deteriorating water quality (above the maximum permissible concentrations) in the tested samples of the water flows in relation to 4 parameters including: iron, manganese, cadmium and copper. Increased concentrations of heavy metals in waterways examined ranged from casual to occasional appearances (iron, manganese and copper) and occasional to frequent occurrences (cadmium). The highest average concentrations of iron were measured in the water of Pchinja River, and lowest in the water of Lepenec River. The manganese was most abundant in the waters of Markova Reka, and at least in the waters of

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Pchinja River. Cadmium was most present in the waters of Lepenec River and at least in the waters of Pchinja River. Copper was the most prevalent in the waters of Markova Reka, and at least in the waters of Pchinja River. The Lepenec River showed exceeding of manganese and cadmium (class III-IV) derived from cement and metal industries from neighboring Kosovo. In Pcinja River was measured exceeding iron (up to class V), cadmium and copper (class III-IV). The source considered industrial facilities in upstream of the Kumanovo region through which the watercourse where increased use of fungicides in agriculture. Markova Reka showed unacceptable concentrations of cadmium, manganese and copper. Besides the State Rules for Classification of river water, for comparison were used also some world experiences as a benchmark for accuracy of water used for irrigation. In this context, the use value of the waters of the surveyed rivers in terms of irrigation is reduced relative to the 7 indicators of heavy metals (Fe, Mn, Cd, Cr, Cu, Zn, Ni) showing exceeded concentrations of environmental correctness of irrigation water. Regarding this, the only satisfactory quality is in the terms of lead.

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