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Heavy metals in water and sediments of the upper course of the river Crn Drim

Тешки метали во водата и седиментите на горниот тек на реката Црн Дрим

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Abstract:

Crn Drim river is the single major outflow of the outstanding Ohrid lake. Surprisingly, data on the presence of heavy metals in waters and sediments for the whole Ohrid watershed are very scarce. This study presents the data on the concentration of heavy metals Fe, Mn, Zn, Cu, Cd and Pb in both waters and sediments collected along the river Crn Drim (including Globochica reservoir), from seven sampling sites in the Republic of North Macedonia.
The concentrations of analyzed heavy metals show good water quality. As far as sediments are concerned the concentrations of heavy metals are low, with the exception of sampling points at the inflows of rivers Labunishka and Vevchanska.
Seasonal dynamics of heavy metals' concentration in waters was also analyzed. Most of the heavy metals showed the lowest concentration in the spring period due to the high water levels. The annual dynamics of Fe and Mn was an exception from this pattern which might be a result of mining activities in the Ohrid Lake watershed.

Key words: Crn Drim river, heavy metals, seasonal changes, water, sediment

Реката Црн Дрим претставува единствен и главен истек од Охридското Езеро. Изненадува фактот што за целото сливно подрачје се објавени многу малку податоци за присуството на тешки метали во водата и седиментот. Во оваа студија се презентирани податоци за концентрацијата на тешките метали Fe, Mn, Zn, Cu, Cd и Pb во водите и седиментот на седум мерни точки по течението на реката Црн Дрим (вклучувајќи го вештачкото езеро Глобочица) во Република Северна Македонија.
Концентрацијата на анализираните тешки метали покажа дека станува збор за чисти води. Слична е ситуацијата со седиментот, каде се утврдени ниски концентрации на тешките метали, со исклучок на локациите на вливот на Лабунишка и Вевчанска Река.
Исто така, анализирана е и сезонската динамика на концентрацијата на тешките метали

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во водите од истите локации на реката Црн Дрим. Кај најголем дел од тешките метали беа забележени најниски концентрации во тек на пролетниот период што се поклопува со највисокиот водостој. Сезонската динамика на Fe и Mn беше исклучок од ваквата динамика што укажува на можноста од влијанието на рударските активности во сливното подрачје на Охридското Езеро.

Клучни зборови: река Црн Дрим, тешки метали, сезонски промени, вода, седимент

Introduction

The pollution of natural ecosystems with heavy metals is global phenomenon. Particularly in the 20-th century, countless thousands of pollutants, including heavy metals, have been produced, and in part released into the environment (Van der Oost et al. 2003). The study of heavy metals pollution is especially important for vulnerable or important lake systems such as Ohrid Lake and its tributaries/outflows.

The presence of metals is an indication of environmental pollution from natural and anthropogenic sources. In aquatic ecosystems metals can enter through different pathways as from atmospheric deposition and erosion, as well as from agriculture, industry and mining direct or indirect input. When heavy metals enter aquatic ecosystems they can be accumulated in sediments, water and organisms that reside there. Moreover, many factors in the environment can trigger the transformation of metals into ions which is the most dangerous form for living organisms (Wojtkowska 2013).

Chemical analyses of water and sediment traditionally have been used as a tool for pollution monitoring and heavy metals accumulation in aquatic biota (Farkas et al. 2001).

Lake Ohrid is the oldest lake in Europe with exceptional biodiversity that is well documented (Spirkovski et al. 2001). However, only few articles concerning the pollution parameters can be found in scientific literature. As regards the heavy metals there are data for the shores of lake Ohrid, especially for the Albanian part of the lake (Malaj et al. 2012; Shehu et al. 2017). Only recently, heavy metals were analyzed in water samples in the Crn Drim watershed area including several sampling points in the upper flow of river Crn Drim, between Ohrid Lake and Globocica reservoir (Vasilevska et al. 2018). Data on heavy metals in two fish species from Crn Drim river were already published (Jordanova et al. 2018) Heavy metal pollution of aquatic ecosystems is worldwide problem with consequences on the aquatic organisms.

The aim of this paper is to present the results on heavy metals' concentration in water and sediments of the upper course of the river Crn Drim in the Republic of Macedonia.

Material and methods

Study area and sampling of water and sediments

The river Crn Drim (Black Drim, Drini i Zi) is situated in the south-western part of the Republic of North Macedonia and represents the main water resource for all water-related activities in that part of the country. The

Tab. 1 List of sampling localities on river Crn Drim

Locality	Notes	N	E
Crn Drim outflow	Immediately after the outflow from lake Ohrid	41°10'29.16"	20°40'42.08"
Daljan	Immediately after the inflow of river Sateska	41°12'23.88"	20°40'18.34"
Lozhani water treatment plant	Immediately after the Lozhani water treatment plant	41°13'27.04"	20°40'06.60"
Vevchanska Reka inflow	Immediately after the inflow of Vevchanska Reka	41°15'14.90"	20°39'10.04"
Labunishka Reka inflow	Immediately after the inflow of Labunishka Reka	41°16'06.86"	20°37'46.70"
Globochica reservoir	At the entrance point of river into the Globochica reservoir	41°15'48.72"	20°38'19.14"
Golema Reka inflow	Globochica reservoir, after the inflow of Golema Reka	41°19'11.92"	20°39'55.12"

watershed of river Crn Drim incorporates both Ohrid and Prespa Lakes with their tributaries from the mountains of Pelister, Bigla, Galichica, Jablanica, Karaorman and Stogovo. The river watershed covers an area of 9209 km^2 which belongs to three countries: Albania, Greece and Macedonia.

River Crn Drim in the Republic of Macedonia it is 45 km long and flowing from Lake Ohrid in the town of Struga and runs north along the Drimkol valley (Fig. 1). After the dam of the hydroelectric power plant near the town of Debar, the river continues in Albania and inflows into the river White Drim.

All of the samples of waters and sediments were collected at 7 localities (Tab. 1) from the main course of river Crn Drim and two from Globochica reservoir during four seasons: autumn (October 2010), winter (February 2011), spring (May 2011) and summer (July 2011).

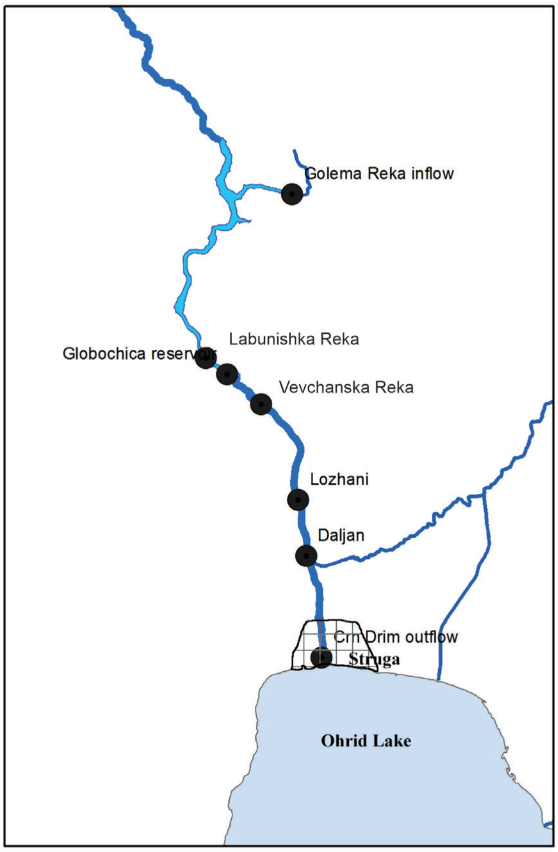

Fig. 1 Study area: Sampling points on the river Crn Drim

Analyses of the chemistry of water and sediments

The preparation of water samples was performed according to Allen (1989). Water samples (500 ml from each location without filtration) were concentrated with 1 ml 'H_2SO_4' and transferred with distilled water in Kjeldahl flasks for digestion. Digestion was performed with HNO_3 and $HClO_4$.

Sediment samples (0.5 g) were wet digested with 8 ml of mixture of HNO_3, H_2SO_4 and $HClO_4$ (10:2:1). This method has very high recoverability rate when used for digestion of plant material (Twyman 2005) and acceptable recovery for digestion of sediments (Idera et al. 2014: over 95% for Pb, Zn, Cd, Fe, Cr and about 90% for Cu).

Digested material of both waters and sediments was transferred with hot distilled water in 25 ml volumetric flasks. Concentrations of Fe, Mn, Cu and Zn were analyzed by flame atomic absorption spectrometry on Agilent 55A. Concentrations of Pb and Cd were analyzed by graphite furnace Agilent 240Z AA (however, Pb in sediments was not analyzed due to the probable low recoverability rates during graphite furnace AAS determination). Same procedure was applied for blanks which were subtracted from the sample results.

Statistical analyses

For statistical analyses Statistica 7.0 for Windows was used. One-way Anova was used in order to analyze the differences between seasons. For correlation analyses Spearman correlation coefficient was applied.

Results and Discussion

The average results on heavy metals' concentration in water and their content in the sediments of the river Crn Drim are presented in Tab. 2 and Tab. 3, respectively. Detailed information on the seasonal changes of water chemistry can be found in Tab. 4.

The concentration of Cu in the sediments of river Crn Drim (Tab. 3) is very similar to the average values for Ohrid-Prespa region, Fe and Zn are higher while Mn shows lower values (Vasilevska et al., 2018).

Seasonal changes in heavy metal concentrations in water do not show some obvious patterns (Tab. 4). The lowest concentrations of the majority of heavy metals were recorded during the spring period as a result of high water level. The exceptions were Fe and Mn that showed irregular patterns throughout the year. The seasonal fluctuations of these two metals might be in relation with the

Tab. 2 Heavy metals in water

Sampling sites	Fe (µg/l)	Mn (µg/l)	Zn (µg/l)	Cu (µg/l)	Cd (µg/l)	Pb (µg/l)
Crn Drim outflow	61.90	6.15	12.34	3.28	0.027	0.091
Daljan	62.30	5.50	18.40	2.97	0.028	0.034
Lozhani water treatment plant	88.04	4.83	29.23	3.01	0.036	0.091
Globochica reservoir	67.85	4.17	14.69	9.89	0.040	0.032
Vevchanska Reka inflow	72.28	4.46	22.78	4.42	0.036	0.040
Labunishka Reka inflow	118.08	34.68	38.25	4.88	0.161	0.073
Golema Reka inflow	63.69	4.94	23.57	3.69	0.098	0.040
Average	**76.30**	**9.25**	**22.75**	**4.59**	**0.061**	**0.057**

Tab. 3 Heavy metals in sediments

Sampling sites	Fe (g/kg)	Mn (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Cd (µg/kg)
Crn Drim outflow	12.23	105.1	82.55	9.75	202.6
Daljan	8.21	56.72	63.33	8.40	113.0
Lozhani water treatment plant	10.13	82.82	87.70	14.50	208.9
Globochica reservoir	22.19	139.1	89.98	17.71	215.2
Golema Reka inflow	18.38	100.5	90.76	16.23	458.9
Vevchanska Reka inflow	21.73	407.7	102.4	30.05	727.8
Labunishka Reka inflow	25.71	252.4	213.3	42.53	834.4
Average	**16.94**	**163.5**	**104.3**	**19.88**	**394.4**

functioning of iron-nickel industrial facility near Pogradec in Albania. Namely, increased values of Fe and Mn (up to 1 mg/l) were found in the littoral waters in Albania (Malaj et al. 2012).

As expected, there were no seasonal changes when sediments were concerned and therefore these data are not presented.

There was no significant correlation between the concentration of the heavy metals in the water and their content in the sediments collected in the investigated localities along the river Crn Drim.

Heavy metals as parameters for water quality of Crn Drim river

The quality of surface waters of Crn Drim river was assessed according to the National decree for classification of waters (Official Gazette of the Republic of Macedonia, No. 18/1999). The National decree already classifies river Crn Drim as category II. According to the concentrations of Cu, Zn, Cd, Mn, Pb and Fe all of the analyzed water samples fall in the purest category I-II (oligotrophic to mesotrophic waters).

The concentration of Cd and Pb in all analyzed water samples from the river Crn Drim were below limits for drinking water according to the EU Council Directive 98/83 (Council of the European Union 1998).

As far as sediments are concerned the content of heavy metals are below the *target values* according to the Dutch Environmental Standards (Hin et al. 2010).

Lake vs. river

The concentration of Fe in surface waters of Crn Drim river varied between 60 and 120 µg/l (Tab. 2). Vasilevska et al. (2018) reported value of 50 µg/l. These values are very similar to the ones obtained for the surface lake waters in the Macedonian part of the shore, but considerably lower than the ones from the Albanian shore of the lake (Malaj et al. 2012). However, the more recent study of Fe concentration in lake surface waters in the Albanian part of the shore showed considerably lower values – 31.2 in µg/l in average for October 2014 (Shehu et al. 2017). Obviously and as expected, the concentration of Fe in Crn Drim surface water is direct result of the status of the lake waters. According to Vasilevska et

Tab. 4. Seasonal changes in the heavy metals' concentration in water of the river Crn Drim

Locality	Season	Fe (µg/l)	Mn (µg/l)	Zn (µg/l)	Cu (µg/l)	Cd (µg/l)	Pb (µg/l)
Crn Drim outflow	autumn	66.40	4.53	14.53	5.12	0.104	0.030
	winter	89.20	5.89	38.52	3.52	0.070	0.049
	spring	50.40	3.31	9.39	2.22	0.012	0.001
	summer	48.75	6.04	31.86	3.91	0.205	0.079
Daljan	autumn	85.75	2.75	21.00	31.34	0.082	0.037
	winter	46.65	3.65	10.21	2.55	0.027	0.045
	spring	47.55	3.90	10.91	2.55	0.014	0.004
	summer	91.45	6.37	16.66	3.12	0.037	0.042
Lozhani water treatment plant	autumn	70.10	5.03	24.23	3.20	0.058	0.028
	winter	50.65	3.17	32.14	4.06	0.036	0.059
	spring	99.95	5.64	8.95	3.16	0.014	0.001
	summer	68.40	3.99	25.78	7.28	0.036	0.074
Globochica reservoir	autumn	75.05	4.18	10.94	3.80	0.031	0.033
	winter	77.40	11.09	21.27	4.41	0.040	0.054
	spring	43.05	4.61	8.55	2.56	0.013	0.015
	summer	52.10	4.73	8.58	2.34	0.025	0.260
Labunishka Reka inflow	autumn	98.30	5.98	54.67	3.79	0.059	0.055
	winter	68.90	4.38	22.01	2.94	0.037	0.194
	spring	101.2	5.85	12.86	2.94	0.015	0.005
	summer	83.75	3.12	27.37	2.37	0.031	0.111
Vevchanska Reka inflow	autumn	162.9	67.84	23.11	5.89	0.119	0.009
	winter	82.55	20.41	49.28	4.77	0.432	0.124
	spring	152.8	24.46	28.73	3.57	0.042	0.011
	summer	73.95	26.02	51.88	5.29	0.051	0.148
Golema Reka inflow	autumn	60.05	7.31	30.77	4.20	0.052	0.030
	winter	109.9	7.46	16.99	2.29	0.028	0.071
	spring	63.55	4.81	10.30	2.71	0.011	0.006
	summer	15.70	2.43	15.53	2.69	0.023	0.027

al. (2018) the concentration of both Fe and Mn in surface waters in lake Ohrid tributaries is a results of the geologic composition of the area. However, they found low value of 18 µg/l for Fe in the tributaries of Lake Ohrid. Thus, we consider the increase in Fe concentration after the inflow of Vevcanska and Labuniska Reka a results of the pollution impact of these two rivers (erosion) and settlements upstream (communal waters).

Similar pattern was observed in the case of Mn. The concentration of Mn in Crn Drim surface waters (Tab. 2) was comparable to the values published by Vasilevska et al. (2018) as well as the values for lake waters in the Macedonian part, but lower than the ones from Albanian shore (Malaj et al. 2012). Again, Mn concentration considerably increased at the point of Vevcanska Reka river inflow. In other tributaries of Ohrid Lake the concentration of Mn was 7.9 µg/l (Vasilevska et al. 2018).

The concentration of Cu in the surface waters of Crn Drim was 4.59 µg/l in average, 3.28 µg/l at the outflow point, and the highest values of over 60 µg/l after the inflow of Veckanska Reka (Tab. 2). Vasilevska et al. (2018) found 13 µg/l of Cu in the waters of Crn Drim river. These values are comparable with the lake's Cu concentration of Shehu et al. (2017). Although sampled in November and December the results of Malaj et al. (2012) are 3-15 fold higher for Cu in lake waters.

The concentration of Pb in the surface waters of Crn Drim river was very low (Tab. 2). These values were considerably lower than the values for the lake waters (Malaj et al.

2012; Shehu et al. 2017).

Cd concentration of Crn Drim waters were higher than the values of Shehu et al. (2017) but lower than the ones of Malaj et al. (2012).

Conclusions

Heavy metals concentration in analyzed samples of waters and sediments of the upper part of the river Crn Drim show that the anthropogenic pressure is low and in general the waters of the river are not polluted with heavy metals. The seasonal dynamics of the concentration of analyzed heavy metals had no obvious pattern although most of the heavy metals had the lowest concentration in the spring period due to the high water levels. The annual dynamics of Fe and Mn was an exception which might be a result of mining activities in the Ohrid Lake watershed.

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