Carpathian Journal of Earth and Environmental Sciences, October 2010, Vol. 5, No. 2, p. 177 - 184

DEGRADATION OF TOPCIDERSKA RIVER WATER QUALITY (BELGRADE)

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Abstract: In this paper a study of degradation of water quality of Topciderska River has been shown. Topciderska River flows through Belgrade city nucleus and presents one of the most polluted rivers in this area, which joins to Sava river upwards from confluence of Sava and Danube. Various techniques have been used such as Ion chromatography (IC), Inductively coupled plasma emission spectroscopy (ICP-OES) and pH measurements, conductonetis and phisical parametars. Anions were analysed with ion chromatography and cations were determined with ICP-OES. The chosen locations in which sampling was done are situated in lower part of Topciderska river. Sediment, as the larges strorage and resorces of heavy metal (HM), plays a rather important role in metal transformations. The pH and HM can directly change metals distribution in sediment; however temperature and conductivity, mainly through changing the pH values, indirectly alters metals distribution. This river is one of the most polluted urban flows in Serbia. It represents good example for studying hydrologic changes influenced by social processes.

Keywords: Topciderska River, chemical degradation, water quality, environment.

1. INTRODUCTION

Rapid development of energetics, industry, transportation, and urbanization as well as constantly increasing population considerably changed balance in the environment. Despite of considerable knowledge and mankind progress, there is a great disproportion between degradation of the environment and measures which should be taken to reduce timily uncontrolled pollution and devastation (Dragicevic et al., 2008). Topciderska River is particulary exposed to polluting substances due to the Rakovica industrial complex, situated within the drainage basin which waste waters flow to the river without refinment. In previous investigations prior attention was given to determination of depositional balance in rivers (Dragicevic, 2002; Dragicevic et al., 2007).

Water pollution is a result of human activity, and demographic characteristics at one side and urbanization and industralization at the other. Nowadays, heavy metals originating from anthropogenic activities are frequently detected in soils, sediments and water columns of river, which cause a considerable number of the world's rivers severely contaminated (Simic et al., 2001; Theofanis et al., 2001; Arribere et al., 2002; Akcay et al., 2003; Olivares-Rieumont et al., 2005; Singh et al., 2005; Lăcătuşu et al., 2007; Damian et al., 2008; Marin et al., 2010). Heavy metals pollution had gradually become a major concern worldwide. In aquatic environment, heavy metal is usually distributed as follows: water-soluble species, colloids, suspended forms and sedimentary phases. However, unlike organic pollutants, natural processes of decomposition do not remove heavy metals. On the contrary, they usually are enriched in sediment by organisms or some other compounds. In some conditions, more than 99% of heavy metal entering into river can be stored in river sedements in various forms (Salomons & Stigliani, 1995; Milivojević et al., 1996, Hajdu & Füleky, 2007).

However, heavy metals cannot fix in sediment forever. With the variation of the physicalchemical characteristics of water conditions, part of these fixed metals will re-enter the overlying water and become available to living organisms. Thus, sediment often acts as both carriers and potential sources for metals in aquatic environment (Theofanis et al., 2001). Heavy metals usually possess significant toxicity to aquatic organisms, and then affect human health through food chain. Therefore, investigating the transformation and distributions mechanisms of heavy metal in sediment becomes necessary. The main purpose of this paper is to provide determination of physical-chemical water parameters in Topciderska river, as well as establishing of these influences on water quality. Ion chromatography (IC) has become a mature analytical method since its introduction by Small et al. (1975) owing to its wide applicability to the determination of ionic species in various water samples.

2. EXPERIMENTAL DETAILS

2.1 Monitoring sites

The area of Topciderska River drainage basin is 147.2 km^2, with the length of 25 km. The average width of the drainage basin is 4/5 of its length, 6.5 km, and it narrows in last 5 km on 2.5 km. According to its basic characteristics this River is considered as a small one. The drainage basin of Topciderska River consist of 24 sub drainage basins, from which according to area that covers and the total length, Duboki potok (36.4 km^2 and 11.2 km) is the biggest one. At the other hand, the smallest sub drainage basin is Radusa (5.1 km^2 and 2.3 km). The total length is 28.1 km, and relative slope is 9.76 %.

Gentle sides are morphologic characteristics of Topciderska River drainage basin with the biggest difference in the altitude between Avala Mountain and the main flow where within the distance of 2.5 km there is the height difference of 390 m with the slope value of 15.6%. The average altitude is 291.5 m, and the average difference in altitude is 119.5 m.

The area of Topciderska River contains both urban and rural parts within the city area. Urban part of it is taking 20 % while rural has 80 % of city area. It means that the rural one is dominant one despite the neighboring city area. From the total area of drainage basin, it has been analyzed 17.5 km^2, nearly 12 %. Erosion production and sediment discharge were calculated for total area of drainage basin. Samples of sediment were taken at lower section of Topciderska river bed. The length of this section amounts to 4.6 km (from confluence into river Sava to local settlement Rakovica, with mean slope of river bed Sm=0.36%).

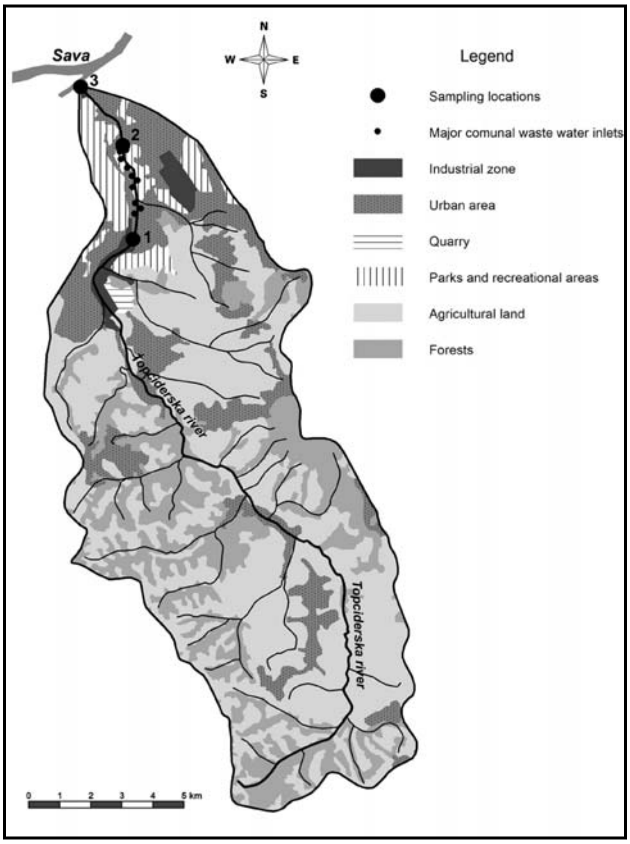

Figure 1. Geospatial characteristics of the field.

2.2 Materials and methods

During the 2008th analysis of water and sediments in the drainage basin of Topciderska River were made and total of 12 samples of suspended sediments and 9 water samples (total 21) in 3 selected locations in drainage basin were taken, after which their physical and chemical characteristics were analyzed. Sampling was conducted at three measuring points, each with three samples. In the water samples 1, 2, 3 taken on june 18th, 1A, 2A, 3A taken on june 27th, and 1B, 2B and 3B taken on july 7th physical-chemical analysis were made also with determination of the concentration of suspended sediment, while the analysis of samples 1C, 2C, 3C that were taken on july 10th determined only the concentration of suspended sediment (Dragićević et al., 2009).

In order to supplement the survey, beside analysis of water samples, also the sampling of the deposited sediment (sludge) on these sites was carried out, with the aim of determining the concentration of heavy metals.

In this study several techniques have been used. Ion chromatography was carried out on Faculty of Physical Chemistry University of Belgrade. Environmental Protectionh Agency (EPA) method 300.1 was used. Inductively coupled plasma emission spectroscopy was done in Vinca Institute of Nuclear Sciences (VINS), Laboratory for Physical Chemistry, Serbia. The method is selected from EPA 200.6.

2.2.1 Chemical analysis

The common anions (Cl^-, PO_4^{3-}, NO_3^-, NO_2^- and SO_4^{2-}) were analysed by ion chromotography (US= EPA method 300.1) with Compact IC, Metrohm. The analytical columns included a Metrosepp A Supp 1. Eluent conductivity was suppressed by an 3 mM Na_2CO_3. Na^+, Ca^{2+}, Mg^{2+}, K^+, Si^{2+}, Cd^{2+}, Pb^{2+}, As^{3+} and Hg^{2+} determined by inductively compled plasma. Analytical emission lines, including background measurement positions and correction of spectral interference, were selected from US Environmental Protection Agency method 200.6. In this investigation SPECTRO spectrofotometer type SpectroFlame was used. The alkalinity of the waters was determined by a potentiometric device Seven Easy pH meter – METTLER TOLEDO with inflection point detection. The values of the physicochemical variables measured at each of the nine sites of the are show in table 1. Also, the analitical results of the waters are show in Table 2,3.

3. THE PARAMETERS OF HYDROLOGICAL CONDITION CHANGES

Topciderska River is regulated from the mouth up to 12.8 km by implementation of urban type of regulation, with prismatic, covered riverbed. At the sector through the part of industrial area Rakovica, riverbed is closed, as collector type. The upstream section of river bed is not regulated, overgrown by shrubs and grass, with reduced capacity for maximal discharge.

Downstream section of river bed, 4.6 km long, is regulated, but in some places with huge amounts of garbage, deposited sediment and spontaneous appearance of shrubs. River regulation is not able to receive and safely carry more water than 78.7 m^3/s, which represents only 61.2% of maximal discharge with return period of hundred years ($Q_{max1\%}$=128.6 m^3/s). The last appaearance of flooding was recorded 9.7.1999, with discharge of 88.58 m^3/s (Dragićević et al., 2009). To Topciderska River could safely receive and conduct big water trough initially projected state and impeccably cleaned and maintained, and this is not the case in the lower part of the course.

Considering the fact that the riverbed of Topciderska River is significantly overgrown with weeds and vegetation that comes to the accumulation of sediment, inevitably that may occur from spills water troughs and a lot smaller than the projected over a hundred years. What can cause degradation it becomes clear after an insight into the chemistry and other characteristics of water and sediment of the flow.

Four categories of erosion are represented in Topciderska river drainage basin, as a result of climate, soil, geology and anthropogenic (land use) conditions: strong, medium, weak and very weak (according to the classification of S. Gavrilovic) (Gavrilović, 1972; Dragićević at al., 2009). Mean annual production of erosive material on drainage basin amounts to Ep=99448.3 m^3 (675.6 $m^3 \cdot km^{-2}$), total sediment discharge in hydrographic network Qs=17266.6 m^3 (117.3 $m^3 \cdot km^{-2}$), bed load sediment discharge Qsbl=21.7 $m^3 \cdot km^{-2}$, and suspended sediment discharge Qss=95.6 $m^3 \cdot km^{-2}$.

Heavy erosion (II category) occurs mainly in the upper part of the basin (7.78% of the total area), on the steep without forest cover, in the form of furrows, sheet erosion and gullies in some places.

Erosion of medium intensity (category III), occurs in the field, as well as areas with steeper slope. It covers 28.80% of the total area of the basin. It occurs mainly in the form of surface erosion. This type of erosion is spread throughout the basin.

Weak erosion (IV categories) occurs in agricultural surfaces (arable land, orchards, meadows) with a gentle slopes, as well as the area under forest. It covers most of the watershed area - 43.75%. The rehabilitation works are applied on pastures and meadows, as well as the erosion control works.

Very weak erosion occurs on stable forest stands. It covers 19.67% of the surface of the basin. In such areas there is no need for erosion control works (mean coefficient of erosion Z=0.38).

The consequences caused by erosive processes in Topciderska river basin can be classified into two basic categories: direct and indirect. The first includes the loss of land due to the attitude, but the loss of the water, which is due to reduction or complete attitude soil cover (no conditions for the accumulation of water after rain or melting snow). In these cases, the water goes in the form of waves flooded, and in much of the government drought. Second are those that result from floods and Neutering plain sandy soil infertile.

Besides mentioned damages that are clearly visible and noticeable, erosion and damages caused by river load in the environment are manifold, as applied, along with suspended in water flows due hydrological network and various chemical substances: organic and mineral fertilizers, pesticides, nutritive elements found in land and all these chemical substances cause water pollution. In this way it becomes unusable for water supply and irrigation, as well as for industrial use.

4. RIVER POLLUTION AS AN INDICATOR OF HYDROLOGICAL CONDITIONS CHANGE

Construction of industrial facilities has not only led to a degradation of natural conditions in the basin of Topcidrska River, but inevitably caused pollution of water. At several places in the industrial zone river flow is completely covered, and what once has been natural watercourse, now is turned into a collector of waste water.

In the last 5 km of the river flow there are even 35 active discharges of pollutants in the river flow. Most of them represent outlets of communal waters, while located near the mouth of the river discharges of large industrial enterprises are located, the NIS (Serbian Oil Industry), and the Coin Mint "Topčider", which are the biggest polluters in this part of the river flow.

Immediately next to the river several important roads pass through. Railway Belgrade-Bar follows the course almost from the mouth of the river and up to ten kilometers upstream. Beside the river in the urbanized part of the valley very active road transport takes place, and there is a set of the tram rails also. Only on the regulated part of the river flow there are 28 bridges for road and rail traffic. All this indicates that the traffic, given the frequency in the lower part of the river valley, is a major source primarily of air pollution, but also directly and indirectly, pollutant of river water. In addition, constant danger of accidental pollution of the river is present, due to traffic accidents, and also from possible leakage of dangerous materia during their transport (March 1988, May 1999, April 2006). Over the river numerous pipelines cross, which further increase the risk of accidental pollution. There is a constant danger that the intensity of river pollution by traffic will be increased, with planned construction of new and expansion of existing roads, which would largely increase frequency of traffic that is taking place close to river flow.

Determination of the degree of degradation required taking of soil and water samples in order to aquirre the amount of pollutants in them (especially heavy metals). This is conditioned by the fact that in the lover part of Topcidrska River zone of heavy industry has been constructed, and also fully or partially urbanized suburbs of the City were built. Water management planning of Topcidrska River drainage basin didn't follow the general trend of urbanization and industrialization, so there are now significant problems due to illegal pollution of watercourse by waste water from urbanized and industrial zones.

Based on the analysis of suspended sediment concentrations, its reduction along the downstream section of river bed was detected, which may indicate the accumulation of river sediment at the mouth of the river, and these statements have already been found in earlier research (Dragićević et al., 2009) with emphasized accumulation of industrial origin waste.

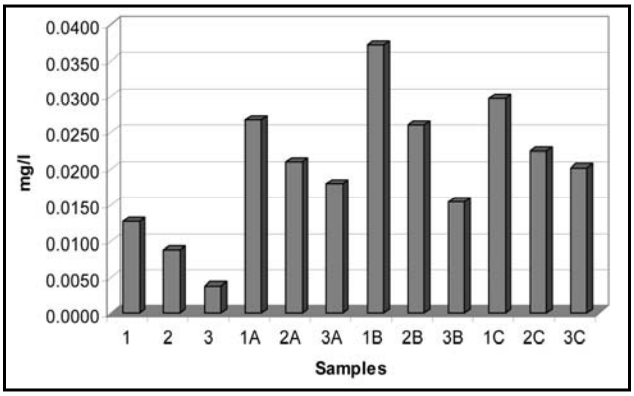

Figure 2. Reduction of suspended sediments concentration along the longitudinal profile

Suspended sediment in hydrographic network unites with various chemical substances (organic and mineral fertilizers, pesticides, nutritive elements found in soil) that cause chemical contamination of water get into, and it thus becomes unusable for water supply, irrigation and for industrial use. On the other hand, it becomes a time bomb which due to the spillage of contaminated water with suspended sediments outside of river bed can cause serious environmental degradation.

5. RESULTS AND DISCUSSION

Values of physicochemical variables measured before starting the experiment in all sites are sumarised in Table 1. These variables are water temperature, conductivity and pH values. Temperature and conductivity decrease downstream, until the pH values are randomly distributed.

Table 1 .Values of the physicochemical variables measured at each of the nine sites.

Site		Temperature (°C)	Conductivity (μS/sm)	pH
1	1A	28,4	800	8,77
	1B	29,3	790	8,81
	1C	29,1	741	8,80
2	2A	26,7	772	7,56
	2B	26,7	784	7,79
	2C	26,7	797	7,87
3	3A	25,5	766	8,47
	3B	24,8	774	8,75
	3C	24,9	771	8,76

Values of anion concentrations in sampled water are presented in Table 2. Concentrations of anions (Cl^- , $PO_4{}^{3-}$, $SO_4{}^{2-}$, NO_3^- , NO_2^-) in riverbed sediment and stream water measured at that time as the environmental baseline condutions are presented in average values for allmethods were exceedingly higherin site 2 in the other two (Table 2). It is clearly seen in table 1 that water temperature decrease downstream from the measuring point 1 to the measuring point 3. On the measuring point 1, sample 1B had the highest temperature value of 29,3°C. On the point 3. in the sample 3B had the lowest temperature value 24,9°C. Measured conductivity values was in the range from 741 μS in the sample 1C, up to 800 μS in the sample 1A.

Lowest concentration value for chloride anions was found in the sample 3A and it was 38,225 mg/l. The highest concentration value had the sample 3B and it was 51,327 mg/l. All values deviates from the highest allowed concentration given by Hazardous Substance Regulations in water "Sluzbeni glasnik RS", No 31/82. Nitrite concentration are in the range from 1,852 mg/l in sample 3B up to 2,606 mg/l in sample 3A. All values deviates from the highest allowed concentration given by Hazardous Substance Regulations in water "Sluzbeni glasnik RS", No 31/82. It is clearly seen in table 2. that the only sample that deviates from maximal allowed concentration is sample 3A. Measured values for phospfate concentration are in the range from 3,455 mg/l in samlple 3B up to 5,819 mg/l for sample 2B. All values deviates from the highest allowed concentration given by Hazardous Substance Regulations in water "Sluzbeni glasnik RS", No 31/82. Sulphate concentrations are in the range from 54,281 mg/l in sample 1B up to 70,548 mg/l sample 1A. Maximal allowed concentration for sulphate anions is not determined by Hazardous Substance Regulations in water.

As it is shown in table 3, concentration of unharmfull oxides (Na^+, K^+, Mg^{2+}, Ca^{2+}) obtained by quantitative analysis are:

1. concentration of Na^+ ions has the lowest value in the sample 1C (31.1±0.6 mg/l) and the highest value in sample 1A (38±1 mg/l);
2. concentration of K^+ ions has the lowest value in the sample 1C (5.7±0.4 mg/l), and the highest value in sample 3A (7.8±0.8 mg/l);

Table 2. Anions analysis.

Sample		Cl^- (mg/l)	$PO_4{}^{3-}$ (mg/l)	N_2O_3 (mg/l)	N_2O_5 (mg/l)	$SO_4{}^{2-}$ (mg/l)
1	1A	39,89	5,413	-	-	70,548
	2A	40,008	5,682	2,315	6,589	57,036
	3A	38,225	3,652	2,606	17,874	55,481
2	1B	39,449	5,323	2,064	6,547	54,281
	2B	41,077	5,819	1,918	5,340	55,364
	3B	51,327	3,455	1,852	7,123	55,022
3	1C	38,766	5,839	2,424	7,829	55,387
	2C	47,541	5,752	2,188	4,306	56,416
	3C	39,819	5,182	1,903	7,262	55,775

*The analitical data of the following iones were below the detection limit 0,020 m.

Table 3. Cations analysis.

Samples		Na^+ (mg/l)	K^+ (mg/l)	Mg^{2+} (mg/l)	Ca^+ (mg/l)	Si^{2+} (mg/l)	Pb^{2+} (mg/l)	Cd^{2+} (mg/l)	Hg^{2+} (mg/l)	As^{3+} (mg/l)
1	1A	38±1	7.6±0.5	25.2±0.8	86±2	5.9±0.5	<0.01	<0.01	0.029	<0.005
	1B	37±1	7.2±0.3	25.4±0.8	88±2	6.0±0.5	<0.01	<0.01	0.018	<0.005
	1C	31.1±0.6	5.7±0.4	26.7±0.8	90±3	5.7±0.5	<0.01	<0.01	<0.002	<0.005
2	2A	35±1	7.1±0.5	27.2±08	100±3	6.9±0.5	<0.01	<0.01	0.014	0.007
	2B	35.08±0.8	7.0±0.5	27.1±0.8	97±3	5.6±0.5	<0.01	<0.01	0.014	0.006
	2C	32.5±0.9	6.6±0.5	26.2±0.8	93±3	4.8±0.5	<0.01	<0.01	0.010	<0.005
3	3A	35.7±0.8	7.8±0.8	24.4±0.8	93±3	6.1±0.5	<0.01	<0.01	0.004	<0.005
	3B	37.0±0.9	7.8±0.7	24.6±0.8	92±3	5.7±0.5	<0.01	<0.01	0.004	<0.005
	3C	33.4±0.8	7.6±0.8	25.9±0.8	99±3	5.1±0.5	<0.01	<0.01	<0.002	<0.005

3. concentration of Mg^+ ions has the lowest value in the sample 3A (24.4±0.8 mg/l), and the highest value in the sample 2A (27.2±08 mg/l);
4. concentration of Ca^+ determined in the sample 2A is 100±3 mgl.

By the Hazardous Substance Regulations in water "Sluzbeni glasnik RS", No 31/82, maximal allowed Pb^{2+} concentration for river class III and IV is 0.01 mg/l. As it is shown in table 3., all determined lead concentrations in the samples are less then 0,01 mg/l, which is ten times lower then the maximal allowed concentration.

On figure 3 the mercury concentrations are shown. Values for measured concentration are in the range from 0,029 mg/l in sample 1.

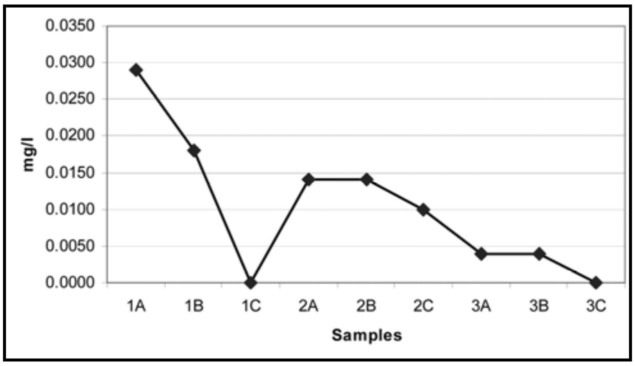

Figure 3. The mercury concentrations in the samples.

The lowest value is determined in the sample 3 (0,002 mg/l). All determined values deviates from maximal allowed concentration more than ten times. The dependence of the concentration of heavy metals in the water, with pH is a clear and well known process (Small, et al., 1975). As the pH increases to values close 8.0, the concentration of the metals decreases, due to precipitation of nitride, sulphates or chlorate. The difference in metal concentration between the polluted (pH<8) and unpolluted samples (pH>8) in several orders of magnitude especially in the case of Zn and Mn, in which a difference of three orders of magnitude was found.

All values for As concentration are less then maximal allowed concentration given by the Law about water. By the Hazardous Substance Regulations in water, maximal allowed As^{3+} concentration for the river class III and IV are 0,05 mg/l. The highest As^{3+} concentration was found in the sample 4. 0,007 mg/l.

In order to supplement the survey, beside analysis of water samples, also the sampling of the deposited sediment on these sites was carried out, with the aim of determining the concentration of heavy metals. The analysis of heavy metals in deposited sediment (sludge) found that all the results are on the border or over the maximum allowed concentration, and it can be particularly alarming (figure 4).

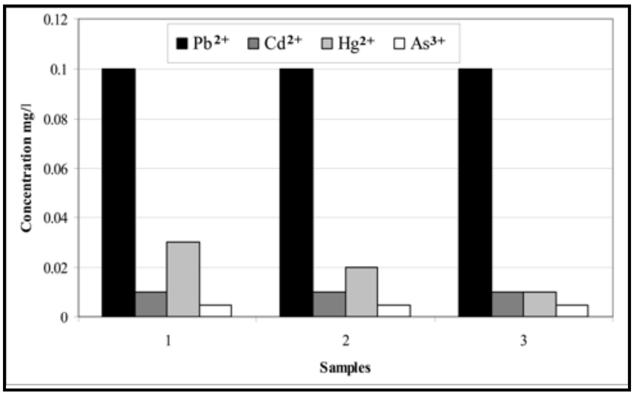

Figure 4. The concentrations of heavy metals in deposited sediment (sludge).

On figure 4, mercury concentration values range from 0.01 mg/l to 0.03 mg/l in the samples, and all the values differ by several tens of times of maximum allowable concentration, that is 0.001 mg/l.

4. CONCLUSION

On the base of the analyzed parametres, the intensity of the pollution (degradation of natural conditions) is changing down the long profile starting from location 1. Thereby, there is no regular decrease or increase of concentration of the analyzed parametres.Temperature of the water decreases from the source of the River towards its confluence. Ph value continualy increases, towards the confluence which is obvious in each of samples on the chosen locations. However, concentration of mercury is constantly higher then allowed value. The highest concentration is by the entrance of the river while downstream concentrations are decreasing. At the other hand, concentration of phosphor is quite interesting and shows considerable increase which may be related to sewage output. The analyses of concentration of heavy metals in river load is alerting because all results are above maximal allowed concentration.

On the base of content and chronology of the investigation it can be noticed that the prime aim of this research was given to determination of recent state as well as to scale of degradation of hydrological conditions of Topciderska River. Carried out investigation presents a starting point for next phase of investigation which includes establishing of degradation scale not only for a river but whole drained area, then making a list of techiques for its sanation and revitalization.

This is influenced by fact that in the lower course of the investigated river a powerfull industrial zone is built as well as few fully and partly urbanized suburbs.

Water-utilized regulation of Topciderska river drainage basin did not follow general trend of urbanization and industrialization, therefore considerable problems came up due to uncommited pollution of this River by waste waters from urbanized and industrialized zones.

The River becomes ecological problem due to flooding of polluted waters which may cause serious degradation of the environment. Considering the fact that Topciderska River bed is significantly covered by crabgrass and vegetation, which may lead to deposition of litter, flooding is necessarily in less probability then in a hundred years. According to analyzed characteristics of the River, it is clear that it may cause considerable degradation.

Topciderska River is only one of the examples from the urban area of Belgrade where majority of streams in last hundred years were assigned to sewage system or left to negligence and misuse. While we are doing degradation of our rivers, big cities from abroad are showing different examples, in terms of restoration and revitalization of their rivers (Chongu-Chong in Seul).

Acknowledment

This work is supported by Serbian Ministry of Science within the projects 43006 and 142016.

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Received at: 22. 02. 2010
Revised at: 24. 07. 2010
Accepted for publication at: 31. 07. 2010
Published online at: 03. 08. 2010