Original scientific paper
UDC: 621.311:631.67(282.24 Sava)
DOI: 10.7251/afts.2015.0713.059P
COBISS.RS-ID 5440280

ASSESSMENT OF WATER QUALITY OF THE PEK RIVER BASED ON PHYSICOCHEMICAL ANALYSIS

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ABSTRACT

Levels of physicochemical parameters (pH, electrical conductivity, sulphates, chlorides, temperature, turbidity, total hardness, iron, manganese, copper, dissolved oxygen, oxygen saturation, total suspended solid, ammonium nitrogen, total nitrogen and orthophosphates) were determined in the water samples collected from Pek River at 4 sample sites during 6 months. Monitoring was done at the source of river, on the border between the municipalities Majdanpek and Kučevo, on the border between the municipalities Kučevo and Veliko Gradište and at the confluence of Pek into Danube River. Some of the physicochemical parameter values fall within national standard and WHO limits, some are not.

Key words: *Pek River, physicochemical parameters, water quality*

INTRODUCTION

Water resources are of critical importance to both natural ecosystem and human development. Good quality of water resources depends on a large number of physicochemical parameters and biological characteristics [1]. Water quality provides the basis for judging the suitability of water for its designated uses and to improve existing conditions. Increasing water pollution due to anthropogenic activities, industrialization, and urbanization causes not only the deterioration of water quality, but also threatens human health and the balance of aquatic ecosystems, economic development and social prosperity [2].

Pek River is tributary of the Danube River and it is located in southeastern Serbia. It empties into the Danube River in the territory of the Veliko Gradište. It is a 129 km long, average water flow is 8.5 m^3/sec. The Pek River originates from two major headwaters, Veliki Pek and Mali Pek. The municipality of Majdanpek has a copper mine which is exploited by the company RBM in Majdanpek, and a factory of copper tubes also located in Majdanpek. According to Šerbula et al. (2015; 2014) in wastewater of the Majdanpek Copper Mine filtration plant (after treatment of wastewater of filtration plant in sedimentation tanks) it was found an increased content of heavy metal ions (Cu, Fe, Mn, Zn, Pb, Cd etc.) [3] and suspended particles [4] that exceed the values of the maximum permissible concentration defined by the relevant Regulation of the Republic of Serbia.

This paper is derived from the results of activities of the project "Joint efforts for the protection and management of the Pek River". The overall objective of this project was the improvement of integrated protection and management of natural resources in three municipalities that share the Pek River basin Majdanpek, Kučevo and Veliko Gradište [5]. In the basin of the Pek River on the territory of three municipalities Majdanpek, Kučevo and Veliko Gradište in the process of developing project "Joint efforts for the protection and management of the Pek River" were identified a large number of illegal dumps, sewage and industrial effluents - the majority of untreated wastewater. One of the activities that have been undertaken in the project was the field and laboratory analysis of water samples described in this paper. The results of the study could be used for improve management options of the Pek River.

MATERIALS AND METHODS

Sampling sites

Water samples were collected separately from each of four sampling sites of the river, spanning a period from November 2011 to May 2012. Table 1. contains data about 4 sampling sites. Measurements were carried out in November (date of sampling 8.11.2011.), December (7.12.2011.), January (23.1.2011.), March (20.3.2012.), April (29.4.2012.) and May (27.5 .2012.).

Table 1. Sampling sites

Sampling sites/Location	Description of sampling sites	Position (Gauss-Kruger)
1	Confluence of Pek into Danube River. 100 km upstream (Veliko Gradište municipality)	x-7542602; y-4956769
2	Below the village Rabrovo near the bridge in Klenj (border between Kučevo and Veliko Gradište)	x-7542186; y-4939968
3	Upstream from the village Blagojev Kamen (border between Majdanpek and Kučevo municipalities)	x-7568371; y-4919751
4	30 meters downstream from the confluence of Mali Pek River and Veliki Pek River (source of river, Majdanpek municipality)	x-7571909; y-4915342

According to data from the Republic Hydrometeorological Service of Serbia (RHSS), there are two measuring stations for monitoring Pek River water quality: Kusići (x-7442909; y- 4952604) and Kučevo (x-7548749; y-4930987). Based on the result analysis of the RHSS for the year 2011, determined quality of water was for Kučevo (3rd class / 4th class of waters) and Kusić (3rd class of waters) [6].

Analytical methods and equipment

For the determination of pH, water temperature, air temperature, dissolved oxygen and oxygen saturation it was used equipment and instruments for field analysis. The following equipment and instruments were used for field analysis: air temperature and pH were measured with a LaMotte pH 5 Series Meter (pH value range 0.0-14.0, accuracy ±0.01, pH and air temperature range 0.0-100.0 °C, accuracy ±0.5 °C) calibrated with buffer solutions pH 4.01, 7.00 and 10.00; water temperature, electrical conductivity, dissolved oxygen and oxygen saturation with a Hach HQ40d Digital Multi-Parameter Meter with automatic temperature calibration (water temperature range 0.0-80.0 °C, accuracy ±0.5 °C; EC range 0.1 μS-200 mS, accuracy±0.5%; DO range 0-20 mg/L, accuracy ±0.01 and oxygen saturation range 0 to 200%, accuracy ±1%). Measurements of other parameters were performed in the laboratory in the Veliko Gradište which is set within the project "Joint efforts for the protection and management of Pek River" [5]. In order to determine sulphates, chlorides, turbidity, total hardness, iron, manganese, copper, total suspended solid, ammonium nitrogen, total nitrogen and orthophosphates a portable laboratory LaMotte Smart Water Analysis, Model SCL-05, with LaMotte Smart2 calorimeter and Spectrophotometer DR 2800 Hach Lange with water analysis kits were used [7,8]. Blanks were run through all experiments to detect any contamination.

For assessment of the quality of water, following regulations were used: Regulations on the parameters of the ecological and chemical status of surface waters and the parameters of the chemical and quantitative status of groundwater, Official Journal of RS, No. 74/2011; Regulation on dangerous substances in the water, Official Journal of SRS, No. 31/82; Regulation on water classification, "Official Gazette of SRS", No. 5/68; Regulation on classification of inter-republic water flows and interstate waters and coastal sea waters of Yugoslavia, Official Journal of SFRJ, No. 6/78 [9-14].

RESULTS AND DISCUSSION

The results of measurement of physicochemical parameters (pH, electrical conductivity, sulphates, chlorides, temperature, turbidity, total hardness, iron, manganese, copper, dissolved oxygen, oxygen saturation, total suspended solid, ammonium nitrogen, total nitrogen and orthophosphates) are presented in Table 2. Water temperature ranged between 3.6 and 12 °C during the time of study, while air temperature was minimum (– 1°C) in December and maximum (27 °C) in May.

The observed pH of Pek River ranged from 7.36 to 8.48, which means that pH of the water is within range of the 1st class of waters according to Regulations on the parameters of the ecological and chemical status of surface waters and the parameters of the chemical and quantitative status of groundwater, Official Journal of RS, No. 74/2011 and Regulation on water classification, "Official Gazette of SRS", No. 5/68 [9-11]. Aquatic organisms are affected by pH because most of their metabolic activities are pH dependent. At extremely high or low pH levels (for example 9.6 or 4.5), the water becomes unsuitable for most organisms. Also even small changes in pH could alter the chemical state and impact of many pollutants in water. The present study shows the normal range of pH and therefore suitable for aquatic environment.

Dissolved ions are responsible for electrical conductivity in water such as chloride, nitrate, sulphate, and phosphate anions, or sodium, magnesium, calcium, iron, and aluminum cations. The maximum electrical conductivity (1325 μS/cm) was observed at location 3 in December and minimum (656 μS/cm) in January at location 1.

The minimun content of total suspended solids (1 mg/l) was observed at locationa 1 and 2 during November, December and April, while maximum value (198 mg/l) was observed in May at location 4. Suspended matter consists of silt, clay, fine particles of organic and inorganic matter, soluble organic compounds, plankton and other microscopic organisms. Total solids can be subdivided into total suspended solids (TSS) and total dissolved solids (TDS). Except sanitary wastewater and many types of industrial wastewater, there are also nonpoint sources of suspended solids, such as soil erosion from agricultural and construction site. As levels of total suspended solids (TSS) increase, a water body begins to lose its ability to support a diversity of aquatic life. Suspended solids absorb heat from sunlight, which increases water temperature and subsequently decreases levels of dissolved oxygen (warmer water holds less oxygen than cooler water). Photosynthesis also decreases, since less light penetrates the water. As less oxygen is produced by plants and algae, there is a further drop in dissolved oxygen levels [15]. Most standards for water quality consider water with a TSS concentration less than 20 mg/l to be clear. Water with TSS levels between 40 and 80 mg/l tends to appear cloudy, while water with concentrations over 150 mg/l usually appears dirty. The nature of the particles that comprise the suspended solids may cause these numbers to vary.

According to the content of suspended solids in the water samples from location 1 and 2 (November, December, January, March, April) belong to the 1st class of water, whereas from location 3 (November, December, January, March, April) belongs to the 2nd class of water [10,11]. Water samples from location 1 (May) belongs to the 2nd class of water, and samples from locations 2 and 3 belongs to the 3rd class of water according to the content of suspended solids. The water samples from location 4 is out of class during all months in which the measurement was done, and have been measured higher content of suspended solids than those concentrations that are allowed to water quality for 4th class of water (100 mg/l). Turbidity is sometimes used as a indirect measurement for TSS. Values for water turbidity were ranged from 0.8 to 11.4 NTU in November; from 1.04 to 167 NTU in December; from 7.65 to 218 NTU in January; from 3.8 to 32 NTU in March; from 2.5 to 138 NTU in April, and in the range of 7.45 to 201 NTU in May. As can be seen in Table 2 the highest TSS and turbidity measured in location 4.

High sulfate content were measured in all the samples, which ranged 260-538 mg/l in November; 234-571 mg/l in December; 163-339 mg/l in January; 254-601 mg/l in March; 245-612 mg/l in April; and 158-310 mg/l in May. The highest content of sulfate was measured at locations 3 and 4. Upon the recommendation of the EU (Directive 98/83/EC) and according to national regulation on hygienic drinking water, content of sulfates in drinking water are limited to 250 mg/l [13]. In the case of the sulfate content in the surface waters there is no permissible level in national legislation. As regards the maximum sulfate concentration in effluents that flow into the surface water, allowed concentrations in different countries vary in the range of 150-2000 mg/l. Dissolved sulfates can be derived from the dissolution of SO_4 minerals; oxidation of pyrite and other forms of reduced S; oxidation of organic sulfides in natural soil processes; and anthropogenic inputs, i.e. fertilizers [16]. Drainage from the mine contributes to increasing the presence of sulphate content in the water due to the oxidation of pyrite ore. Oxidation of pyrite may cause acidification of natural water because of acidic water from metal mines or coal mines. However, in the case of the Pek River acidification has not occur, because the measurements showed that observed pH of Pek River ranged from 7.36 to 8.48, which means that pH of the water is within range of the 1st class of water.

The observed total hardness was ranged between 17.8 and 39.8 ° dH. The hardness of natural waters depends mainly on the presence of dissolved calcium and magnesium salts.Water having hardness value in the range 18-30 ° dH are hard water, while the water having a hardness above 30 ° dH are seen as very hard water. Water samples from locations 1 and 2 belong to hard water and water samples from locations 3 and 4 belong to the hard and very hard water. According to the content of chloride, Pek River may be classified as 1st class of water [9] at all locations.

The values of dissolved oxygen (DO) range from 9.53 to 12.7 mg/l. The lower value of DO could be attributed to the presence of biodegradable organic matter. When DO is used as the parameter for water status evaluation, Pek River may be classified as 1st class of water [9-11] at all locations. According to Regulation on water classification Regulation on classification of inter-republic water flows and interstate waters and coastal sea waters of Yugoslavia [11], waters of the 1st class have oxygen saturation which ranges between 90 and 105, waters of the 2nd class have oxygen saturation which ranges between 75 and 90, and oxygen supersaturation which ranges between 105 and 115. When oxygen saturation is used as the parameter for water status evaluation, Pek River may be mainly classified as 1st class of water, except for samples from November at all locations, samples from December at locations 1 and 3, sample at location 1 from April, and sample at location 4 in May.

The observed concentrations of heavy metals (iron, copper and manganese) differ significantly between sampling sites. Concentration of iron, copper and manganese ranged between 0.02-1.26 mg/l, 0.08-3.19 mg/l and 0.052-4.443 mg/l, respectively. According to Regulation on dangerous substances in the water [12], waters of the 1st and 2nd class may contain maximally 0.3 mg/l of iron and 0.1 mg/l of copper, while waters of the 3rd and 4th class may contain maximally 1.0 mg/L of iron and 0.1 mg/l of copper. The level of metals are more pronounced at location 3 and 4 due to the proximity of the copper mine in Majdanpek. The content of dissolved iron in the water at locations 1 and 2 in the samples collected in every month was present in an amount corresponding to the 1st and 2nd class of waters, while at the location 3 the samples collected in the January, March, May content of iron was in amount corresponding to 3rd and 4th class of waters. In the samples collected in December and April, the content of dissolved iron in the water was in an amount that exceeds the iron content determined for 3rd and 4th class of waters. The content of dissolved iron in the water at the location 4 in the sample collected in November belongs to the 3rd and 4th class, while in samples collected in all other months iron was present in an amount that exceeds the iron content determined for 3rd and 4th class of waters [12].

The content of dissolved copper in the water at all sites in the samples collected in November and December is present in an amount that exceeds the copper content specified for 3rd and 4th class of waters. In samples taken in January, March and May, the copper content exceeds the maximum allowable concentration defined for class 3rd and 4th at locations 3 and 4, while at locations 1 and 2 recorded amount of copper belongs to 1st and 2nd class of waters. In April, the copper content exceeds the maximum allowable concentration defined for 3rd and 4th class at sites 2, 3 and 4, while at location 1 recorded amount of copper corresponds to 1st and 2nd class of waters. [12].

Table 2. Concentration of different water quality parameters at 4 sample sites during 6 months

No.	Parameters	Sample site	Nov	Dec	Jan	Mar	Apr	May	*Min*	*Max*
1	Water temperature in °C	1	8	6	4.8	6.7	10.1	12	*3.6*	*12*
		2	8.6	6	5.7	6.8	11	11		
		3	8.8	3.6	3.7	5.5	10.4	11		
		4	8.8	4.4	4.4	6.5	8.7	9		
2	Air temperature in °C	1	12	1	8	11	24	26	*– 1*	*27*
		2	14	2	8	12	23	27		
		3	15	0	9	10	20	26		
		4	13	-1	8	9	17	23		
3	Electrical conductivity in µS/cm	1	833	839	656	820	750	789	*656*	*1325*
		2	870	874	661	881	832	860		
		3	1288	1325	910	1112	980	1090		
		4	1046	1267	812	950	870	930		
4	Total suspended solids in mg/l	1	1	1	6	3	1	14	*1*	*198*
		2	1	1	6	4	1	17		
		3	15	13	12	11	13	34		
		4	167	156	162	148	162	198		
5	Chloride in mg/l	1	13	12	1.26	11	11	2	*1*	*14.5*
		2	7	6.32	1	6	6	2.3		
		3	14.5	7.97	2.36	8.1	8.1	3.8		
		4	11	7.89	5.14	12	8	6		
6	Total hardness in ° dH	1	24	23.1	18.4	25	23	22	*17.8*	*39.8*
		2	28	26.4	17.8	27	25	24		
		3	39.8	34.5	26.1	28	23	23		
		4	33	41.7	18.4	30	34	31		
7	Dissolved oxygen in mg/l	1	11.91	10.55	11.75	11.75	10.45	11.2	*9.53*	*12.7*
		2	12.7	12.12	11.25	11.5	12.2	11.9		
		3	9.53	11.73	11.33	11.48	11.67	11.45		
		4	10.18	11.85	11.65	11.8	11.56	10.3		
8	Oxygen saturation in %	1	106	88	94	94	88	96	*85*	*106*
		2	105	103	94	94	98	103		
		3	85	87	89	92	94	94		
		4	90	94	94	97	98	89		
9	Turbidity in NTU	1	1.03	4.2	7.65	3.8	2.5	7.45	*0.8*	*218*
		2	0.8	1.04	9.25	6	5.1	9		
		3	3.21	20.6	14.1	10	7	12.1		
		4	11.4	167	218	32	138	201		
10	Total nitrogen in mg/l	1	1.5	1.58	2.8	1.9	1.6	2.3	*1.01*	*2.8*
		2	1.2	1.01	2.12	1.45	1.3	1.98		
		3	1.36	1.77	1.85	1.2	1.82	1.43		
		4	2.1	2.39	1.89	1.25	2.15	1.56		
11	Ammonium nitrogen in mg/l	1	0.011	0.011	0.105	0.132	0.015	0.098	*0.011*	*0.717*
		2	0.123	0.121	0.18	0.231	0.13	0.156		
		3	0.576	0.538	0.395	0.421	0.61	0.267		
		4	0.717	0.684	0.489	0.538	0.692	0.389		

12	Orthophosphates in mg/l	1	<0.005	<0.005	0.01	<0.005	<0.005	0.01	*0*	*0.21*
		2	<0.005	<0.005	0.016	<0.005	0.01	0.016		
		3	0.05	0.02	0.03	0.03	0.02	0.03		
		4	0.188	0.171	0.231	0.21	0.15	0.134		
13	Sulphates in mg/l	1	260	234	183	254	245	178	*163*	*612*
		2	298	287	163	307	293	158		
		3	538	571	339	601	612	310		
		4	403	535	247	561	567	198		
14	pH	1	8.08	8.13	8.1	8.02	8.12	8.08	*7.36*	*8.48*
		2	8.15	8.21	8.06	7.95	8.02	7.98		
		3	7.89	8	8.05	8	8.1	7.98		
		4	8.4	7.36	8.48	8.4	8.2	8.1		
15	Manganese in mg/l	1	0.06	0.07	0.06	0.06	0.06	0.08	*0.05*	*4.44*
		2	0.06	0.05	0.09	0.71	0.10	0.12		
		3	0.88	3.15	0.55	0.81	0.63	0.59		
		4	1.07	4.44	0.95	1.23	0.88	1.0		
16	Copper in mg/l	1	0.15	0.11	0.09	0.11	0.09	0.11	*0.08*	*3.19*
		2	1.1	1.41	0.04	0.08	1.12	0.08		
		3	3.19	2.76	0.77	0.9	1.32	0.87		
		4	2.1	3.15	0.8	1.4	1.45	0.91		
17	Iron in mg/l	1	0.02	0.03	0.14	0.08	0.06	0.12	*0.02*	*1.26*
		2	0.02	0.02	0.31	0.19	0.12	0.28		
		3	0.2	1.2	0.51	0.44	1.1	0.46		
		4	0.59	1.8	1.26	1.05	1.3	1.2		

In the case of the manganese content in the surface waters there is no permissible level in national legislation. The allowable upper limit for manganese in drinking water by the Regulation on hygienic correctness of drinking water [13] is 0.05 mg / l, while the WHO recommendations to a maximum of 0.4 mg / l. The manganese content in the samples ranged from 0.06 to 1.07 mg / l in November, ranged between 0.05 and 4.44 mg / l in samples taken in December, ranged between 0.06 and 0.95 mg / l in samples taken in January, ranged between 0.06 and 1.23 mg / l in samples taken in March, ranged between 0.06 and 0.88 mg / l in samples taken in April and ranged between 0.08 and 1.0 mg / l in samples taken in May. The highest amount of manganese was detected at sites 3 and 4.

Copper mine in Majdanpek produce wastewater through which losses a considerable amount of copper ore in soluble or insoluble form. The partially purified wastewater from the concentrate filtration plant is discharged to the Veliki Pek river. Surface and underground water forming Pek and Veliki Pek river flows through the area which are composed of copper, iron, zinc and others elements and thereby increase the concentration of these elements in the water [3]. Šerbula et al. (2014; 2015) compared chemical analyses of wastewater in Majdanpek copper mine and influence of wastewater to the water quality of Veliki Pek river for the period from 2008 to 2012. They concluded that in earlier years impact was greater and that in recent years situation is better because copper mine Majdanpek worked hard to improve the quality of wastewater, and thus to reduce pollution [3,4]. In order to avoid large losses of copper through wastewater, Šerbula et al. (2015) proposed to complement the existing wastewater treatment. For reducion of concentrations of heavy metal ions in the wastewater of the filtration plant could be used various adsorbents such as ion exchange resin. On that way copper would be transformed into copper sulfate and could be used in the Electrolytic Refining Plant in RTB Bor, thereby copper recovery would be complete. Also Šerbula et al. (2014) proposed that for reduction of the concentration of suspended solids in wastewater of the filtration plant could be used coagulants aluminum sulfate, aluminum chloride and sodium aluminate in the sedimentation tanks for gravitational purification before discharging wastewater to the Veliki Pek river [3,4].

Nutrient pollution causes excess algae growth, a type of pollution called eutrophication. The main sources of nitrogen compounds in water are fertilizers, animal waste and sewage. Total nitrogen includes all forms of nitrogen in water sample, such as nitrate, nitrite, ammonia and organic nitrogen. Due to the lack of the permitted level of national legislation for the content of total nitrogen (TN) it was used International Commission for Protection of Danube River (ICPDR) recommendations [14]. According to the ICPDR criteria of water with the maximally content of total nitrogen of 1.5 mg/l belong to the 1st class, and the water that have a total nitrogen content in the range of 1.5-4 mg/l belong to 2nd class. The content of total nitrogen in water samples ranged from 1.01 to 2.8 mg /l, on the basis of which it can be concluded that the water of the Pek River does not contain high concentrations of total nitrogen.

Waters of the 1st and 2nd class may contain maximally 0.05 mg/l and 0.1 mg/l of ammonia nitrogen (NH_4-N) [9,12]. The values of NH_4-N in samples taken from the location 1 (November, December, January, April and May) belong to the 1st class, while the sample was sampled in March belongs to 2nd class of water. The values of ammonium ions in the samples taken from the location 2 in all the months belong to 2nd class. The values of NH_4-N in the samples from location 3 in May belong to 2nd class, while samples taken in November, December, January, March, and April belong to 3rd class. The values of NH_4-N in the samples taken from the location 4 for all months can be classified into class 3rd.

Orthophosphates, also known as reactive phosphates, are a main constituent in fertilizers used for agriculture. It can be carried into streams, river and lakes through run-off. Orthophosphates found in natural water provide a good estimation of the amount of phosphorus available for algae and plant growth. This is the form of phosphorus that is most readily utilized by biota. Concentrations of orthophosphate in the water samples were varied and ranges from 0 to 0.23 mg /l. It was registered elevated concentrations of orthophosphate in the location 4, while values of orthophosphate in the samples taken from locations 1 and 2 in all the months belong to the 1st class. Values of orthophosphate in the samples taken from the location 3 in all the months belong to 2nd class. Values of orthophosphate in the sample sampled from location 4 in May belong to 2nd class, samples taken in November, December and April belong to 3rd class, while the values of orthophosphate in the samples taken from location 4 in January and March belong to 4th class.

According to data from the RHSS [6], it could be concluded that the water quality of the Pek River, at the existing two measuring stations, did not meet the requirements of the 2nd class water quality. Suspended solids at monitoring stations Kučevo and Kusić profiles are occasionally corresponded to 3rd class and 4th class of waters. The values of the percentage of oxygen saturation of water in each series of tests on both profiles fit the 3rd class quality (supersaturation). The obtained values of nitrite (NO_2-N) in one series per tests on both profiles matched the 3rd class and 4th class of waters quality. From dangerous and harmful substances in certain series of test registered elevated content. It was registered increased value of phenol index (3rd class / 4th class) and high content of Zn (3rd class / 4th class) and Mn [6].

CONCLUSION

According to the Regulation water classification, "Official Gazette of SRS", No. 5/68 [10], Pek River is classified into the 2nd class of water quality which is suitable for bathing, recreation and water sports. Based on the results from this study it could be concluded that the water quality of Pek River significantly depends on sampling sites. In locations 1 and 2 the quality correspond to the 1st and 2nd class except for copper content. The results of physicochemical analysis showed that copper and sulphates were present in almost all water samples in exceeded values. It was registered elevated concentrations of iron, copper, manganese, total suspended solids, turbidity, ammonium nitrogen and orthophosphate in locations 3 and 4.

Therefore it is necessary to take appropriate preventive measures in order to prevent further pollution of the Pek River and to improve the current situation. For example applying coagulants in the sedimentation tanks for gravitational purification and ion exchanger will reduce adverse effects of wastewater of the Majdanpek Copper Mine filtration plant on recipient Veliki Pek river and a reduction loss of copper concentrate. Also, it is necessary to examine the impact of other sewage and industrial effluents to the water quality of Pek River. It is necessary to develop utility infrastructure in all settlements in the Pek watershed, including construction of sanitary landfills and wastewater treatment systems to treat wastewaters from households and commercial entities.

This research was financially supported by project "Joint efforts for the protection and management of the Pek River", IPA 2007, 07SER01/02/41, 2011.

(Received April 2015, accepted April 2015)

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