SHKUMBINI RIVER WATER QUALITY

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Abstract

Shkumbini river is the main source of drinking water and fulfill the agriculture and industrial needs for e great population in central Albania as well. The objective of this study was to evaluate the quality of river water based on physical-chemical parameters such as T, pH, TDS, TSS, Ca^{2+}, Mg^{2+}, K+, Na+, Cl-, CO_3^{2-}, HCO_3- and SO_4^{2-}, nutritional elements ($N\text{-}NO_3^-$ $N\text{-}NH_4^+$ and P- PO_3^{4-}) and heavy metals concentartion (Fe, Pb, Cr, Cu, Ni, Zn and Mn). Monitoring was realized during a three years of period 2009-2012. Sampling was carried out at three monitoring stations at about 20 km of distance during the river stream with a four times per year frequency. Nitrogen ($N\text{-}NO_3^-$, $N\text{-}NH_4^+$) and phosphorus ($P\text{-}PO_4^{3-}$) in water were measured using UV-VIS spectrophotometry, following the standard methods recommended by APHA (1985). Heavy metals in all samples were analyzed by Atomic Absorption Spectrometry (AAS) using a Varian SpectrAA 20 instrument. The analytical results obtained were in generally within the accepted values set by the State Standard Catalogue, with the exception of TSS as result of a great erosion, and N- NO_3^-, P- PO_4^{3-} values in S2 as result of massive urban discharging. The content of heavy metals in the Shkumbini river follows the order: Cr>Cu>Ni>Mn>Pb>Fe>Zn, and were within EU norms for these concentrations with a slight decreasing tendency. Our results indicate that Shkumbini rivers water can be considered of good quality (class II). Anyway, since these river is continually threatened by urban, industrial and agricultural pollution, it is recommended to maintain a permanent monitoring program of the water quality.

***Keywords*:** Shkumbini water quality, chemical parameters, heavy metal, concentration

Introduction

Shkumbini river is one of the major and one of the mos important rivers of the country. It flows for 181 km in the center of Albania, with a draw of 2444 km2 [7]. A significant impact on the water quality of this river is rappresented by the spills of the Metallurgical Combine of Elbasan, the spills of the towns and villages that lie in his valley and by the fertilizers used in the agriculture. These factors have acted before strongly before the 1990-s. After the collapse of the system in 1990, the factorys of the combine were closed or reduced the maximum work for a period of 10-15 years [10]. Also agriculture became less intense and this was associated with an improvement in water quality. In the last decade the Shkumbini valley,

due to socio-economic changes but also very favorable geographical position, but also by the partly almost ready infrastructure for industrial activity, mainly metallurgical, is facing a demographic growth and reactivation of some industries. This increase is associated with the increased demand for potable and industrial water, which is associated with the negative impact of the above factors on the quality of the river water. There are also displayed and strongly influencing the young factors that weren't influencing too much before, such as increasing erosion due to massive deforestation and leakage from collection of massive of urban waste due to the concentration of population and growth and diversification of the consumption. In these conditions it needed a continuous control and monitoring of the quality of the water of the Shkumbin river, who is recently threatened by these factors. The purpose of this paper is the evaluation of the quality of the water of the Shkumbin river for 2009-2012, based on the general physico - chemical parameters and the concentration of some nutrients and the levels of heavy metals. There are also considered more the factors which mostly affect the quality of the water and some recommendations for maintaining and improving the quality of the water of the river.

Materials and methods

Sampling stations were set as follows: S1 (Labinot-field) about 12 km away from the city of Elbasan where human impact is considered minimal; S2 (Paper) after untreated urban and industrial spill sites, and S3 (Peqini) about 35 km away from Elbasan along the stream of the river.

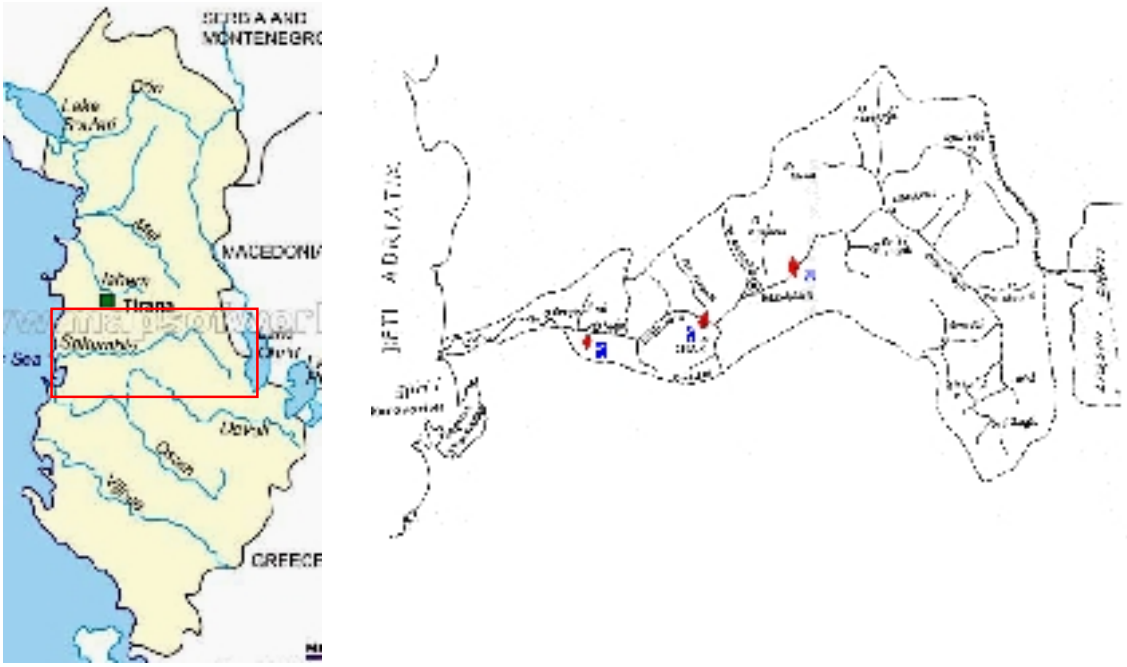


Figure1 : Watershed of Shkumbin river and sampling stations

The samples for the analysis were taken in the period of May 2009 - June 2012, with a 3 monthly frequency. Water samples were taken at 30 - 50cm depth, polytheni in 500ml bottles, in accordance with the standard operating methods [11, 12]. The samples for the analysis of heavy metals were treated with H_2SO_4 to pH 2 in order to eliminate losses.

Temperature, pH, conductivity, dissolved solids (TDS) and dissolved oxygen (DO) was measured directly with camera multimeter Hach (Sension 156). The suspended solids (TSS) was determined after filtration on Whatman filter glass with 0:45 μm membrane. The concentration of nutrients (NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}) was performed with UV - VIS spectrophotometer PYE UNICAM SP6 - 550, respectively at 543nm, 220 - 270nm, 630nm and 880nm. The samples were previously chemically treated with the appropriate reagents for returning to the active form as needed. Heavy metals were determined by Spectroscopic method of Atomic Absorption (SAA) with the Varian spectrophotometer SPECTRA 20 +, in the nitrous oxide flame (N_2O) – at the Ferry Laboratory Factory of Elbasan..

Results and discussion

Physicochemical parameters

The values of physico-chemical parameters: pH, DO, TDS, TSS, for the period of May 2009-May 2012 for three monitoring stations are given in Table 1.

Table 1. The values of physico-chemical parameters of the water quality

	pH			DO, mg/L			TDS mg/L			TSS, mg/L		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
(May 09)	8.0	7.8	8.0	9.4	9.1	8.8	98.0	122.0	145.0	131.0	172.0	158.0
(Agus 09)	8.5	8.1	8.2	8.2	7.7	7.6	178.0	225.0	220.0	48.0	65.0	59.0
(Nov09)	8.1	8.2	8.4	9.3	8.9	8.2	180.0	202.0	221.4	328.0	364.0	475.0
(Febb 10)	7.9	7.8	8.0	9.6	9.1	8.4	65.0	89.0	85.0	175.0	165.0	189.0
(May 10)	8.4	8.5	8.4	9.7	9.2	8.5	104.0	167.7	181.8	95.0	89.0	104.0
(Set.10)	8.6	8.0	8.3	9.1	7.9	7.1	161.7	198.8	198.8	65.3	42.5	78.4
(Nov 10)	8.2	8.2	8.2	9.8	9.6	8.9	47.6	68.3	135.7	375.4	349.2	492.0
(March 11)	8.1	7.9	8.2	9.6	9.3	9.0	124.0	128.0	148.0	145.0	137.0	162.0
(June11)	8.3	8.4	8.3	9.2	8.8	8.4	160.0	184.3	192.0	94.0	78.0	135.0
(Agu 11)	8.3	8.1	8.2	8.5	8.2	7.8	195.0	201.0	265.0	75.0	81.0	69.0
(Nov11)	8.4	8.2	8.3	9.4	8.6	8.4	89.0	98.0	92.0	225.0	254.0	239.0
(Febb 12)	8.3	8.4	8.4	9.8	9.0	8.5	132.0	158.0	162.0	178.0	189.0	184.0
(June12)	8.3	8.2	8.3	9.5	9.1	8.5	111.0	138.2	176.0	125.0	137.0	142.0
Average	8.3	8.1	8.2	9.5	9.0	8.4	126.6	152.3	171.0	158.4	163.3	191.3

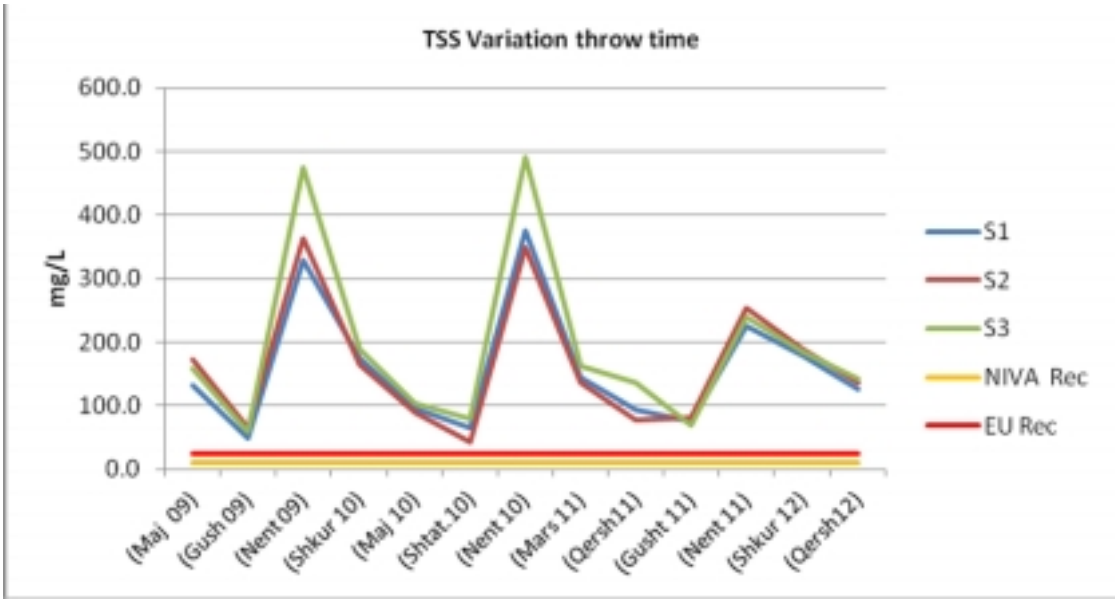
The temperature values vary from season and during the course, but in any case they remain within the limits that support fish life (10 to 21^{o}C) [5].

PH values ranging from 7.8 to 8.6 within the EEC Directive (6-9), but higher than the water level of the first quality classification NIVA (pH > 6.5).

The dissolved oxygen (DO) is a very important parameter of the water quality, since it means"health"of the aquatic environment. DO values vary from 7.1 to 9.8 mg/L and prove that the quality of the water of the Shkumbin river belongs to the first category according to NIVA classification [4].

The dissolved oxygen values represent an insignificant variation of the time, while suffer a slight decline during flow (S1<S2<S3), a decrease caused by sewage discharges of untreated urban waste of the major cities.

A completely different situation is given on the Suspended Solids (TSS). These values exceed any limit to three sampling stations and also represent a high variation during the time (almost 8 times more for S1 in August 2009- November 2010). These particularly high value can be explained by the numerous precipitation preceded the aforementioned period. However NIVA 's guidelines for quality V - waters recommend TSS values below 10 mg/l [4] and those of EU 25mg/l [5] while our averages vary between 57.3 mg/l in 2009 summer and 405mg/l in 2010 autumn (Graph 1).



Graph 1: TSS Variation values throw time according to the stations

Extremely high values of TSS content show a very high erosion of land in the watershed of Shkumbin. According to some studies it result that the erosion in our country is at 20 tons/ha/year, or about 60 million tons of granular solid substance discharged into the sea every year [13]. Factors that lead to such high values are natural geographical factors (sloping territory about 25%) [7], geological (sedimentary geological formations and morphological) [7], climate (average annual rainfall of about 2000mm and high intensity) [13], and human factors such as massive deforestation of the watershed of the Shkumbini River or intensive agriculture.

The concentration of nutrients

The values of the concentration of nutrients accordin to the stations is provided in Tab 2. The quality of the water of the Shkumbin river classified as ”good” (II Class according to NIVA) with regard to these parameters [4].

Table 2. The values of concentration of nutrients

	NO_2^- (μg/L)			NO_3^- (mg/L)			NH_4^+ (mg/L)			PO4 (μg/L)		
	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
(May 09)	3.0	9.0	12.0	0.78	1.02	0.71	0.66	0.38	0.77	32.5	11	9
(Agus 09)	4.5	8.2	14.1	0.21	1.42	1.8	0.18	0.32	0.56	14	17	21
(Nove 09)	19.0	64.0	12.0	3.57	4.8	4.62	0.54	0.42	0.18	12	28	250
(Febb 10)	14.0	31.2	18.4	1.1	2.62	3.1	0.04	0.12	0.11	44	58	89
(May 10)	3.0	15.0	22.0	0.42	0.82	0.75	0.1	0.18	0.21	4	12	28
(Sept 10)	1.2	7.5	6.9	0.14	0.42	0.64	0.12	0.2	0.2	6	32	19
(Nov 10)	3.0	61.0	20.0	0.5	1.14	0.6	0.03	0.12	0.09	30	120	90
(Marc 11)	8.0	19.0	28.0	2.8	3.4	2.86	0.21	0.47	0.44	37	64	56
(June 11)	1.0	5.0	3.0	0.19	0.26	0.23	0.01	0.08	0.06	0	8	12

(Agus 11)	2.1	5.8	6.0	0.34	0.87	1.12	0.04	0.09	0.11	2.6	11	18
(Nove 11)	4.0	37.0	28.0	0.45	0.95	0.88	0.05	0.18	0.13	45	62	84
(Febb 12)	2.0	8.0	4.0	0.21	0.34	0.29	0.01	0.04	0.05	3	9	14
(May 12)	4.8	29.0	15.0	0.89	1.4	1.16	0.19	0.36	0.22	17.6	34	58
Average	5.4	23.1	14.57	0.89	1.50	1.44	0.17	0.23	0.24	19.05	35.85	57.54

The average concentration of N - NO_3^- is between 1:50 and 0.89 mg/L, almost twice less than 2.63mg/L, which is in average about 654 in the european rivers [6]. The presence of nitrites (N - NO_2^-) is an indicator of sewage pollution of the river water, but there are limits to their content in sweet water. Higher values of the concentrations of NO2 - and NO_3^- per station (S2) are due to raw sewage discharges of large urban centers inhabited (130,000 Elbasan inhabitants, Cërrik 15000, etc.) [15].
The ammonia concentration NH4 + (0:17 to 12:24 mg/L) results slightly higher than the 0:16 mg/L (N-NH_4^+) which is the recommendation of the ECC for ciprinide waters, but quite lower than the average 0.66 mg/L reported for 580 monitoring stations in the European rivers [5].
The concentration of phosphates P-PO_4^{3-} (19-59 μg/L) appear below the ECC recommendations levels for salmonid waters (65.3 μg/L P- PO_4^{3-}) [5]. The upward trend from S1 to S3 is caused mainly by the urban effluent and partly from intensive agriculture that is developed in this part of the valley.

Levels of heavy metals
The values of concentrations of heavy metals in the river water are generally low. No record exists about water contamination of these metals. Intervals (min-max) in which concentrations of metals vary between sites is given in Tab 3.

Table 3: Intervals of concentration (μg/L) of heavy metals by stations

	Fe	Mn	Zn	Ni	Cr	Cu	Pb	Cd
S1 (Labinot)	570-800	20-85	2-16	8-24	4-8	0.5-2.8	0.4-1.4	0.0-0.2
S2 (Paper)	624-1460	24-170	4-18	10-35	5-7.8	1-3.2	0.4-2.4	0.0-0.6
S3 (Rrogozhine)	780-1300	40-140	4-20	10-43	4-7.6	1.1-3.2	0.6-2.5	0.1-0.4

There are observed slightly higher values for S2 and S3 which we think are due to increased industrial activity, mainly black metallurgy, which discharge waste into the river. Nevertheless, we have to consider the fact that the analysis of heavy metals in the river water is relatively difficult due to relatively low levels, often near the limits of detection, which may affect the accuracy of measurements. Based on the NIVA classification the water of Shkumbin is classified class I (good). Even here the influence of human factor is present.

Conclusions

The situation of the quality of water of the Shkumbin river based on physico- chemical parameters and the concentration of nutrients in general result ”good”.
As regards the levels of T, pH, DO and TDS of the water quality of Shkumbin result ”good” to ”very good". Critical levels rappresent only the suspended solids TSS, whose values exceed any limit. Natural factors such as the slope of the territory, the level and intensity of high rainfall combined with massive deforestation leading to massive erosion which is the cause of the high values of TSS.

Concentration levels of nutrients are generally within the norms of the European Community, but according to NIVA are classified as class II or partially polluted. Higher levels of N-(NO^{2-} -NO^{3-}) and P – PO_4^{3-} registered for S2 and S3 which are immediately near to the major urban centers are a result of human activity (discharge of untreated urban and industrial effluents and intensive agricultural activity).
The concentration levels of heavy metals keep the water quality of the river Shkumbin within the same class of quality (class I, or ”good” according to NIVA), but still threatened by human activity. This situation is satisfactory although requires a constant monitoring.

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