

Impact of Economic Activities in Water Quality of Erzeni River

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Received: 15 March 2019
Accepted: 20 September 2019

Abstract

The aim of this paper is to assess the impact of the increasing economic activities in one region of Erzeni River basin to the river water quality. The monitored rivers segment of almost 20 km, consisted of less populated areas at the upper stream of river, as reference, and also of areas with intensive economic, agricultural and human activities. The samples were collected from four stations in the course for several months and fourteen physico-chemical parameters were analyzed using standard methods. Based on data analysis, the evaluation of the overall water quality status has been accomplished.

The statistical assessment of the physico-chemical parameters measured and the use of the Water Quality Index (WQI) Methodology clearly showed the deterioration of water quality in the river segment under investigation from upper (S1) to the bottom part of it (S4). The downgrading of calculated WQI alongside the river, from 95.4 to 83.8 indicates the negative impact over the river water quality, imposed by economic activities established in the area.

Keywords: Physico-chemical parameters, human impact, Erzeni River, Water Quality Index (WQI)

INTRODUCTION

Protection of river water quality, as a vital source in development of nations and sustenance of life, is an important and sensitive issue. The experience has shown that “when environmental resources are degraded, the security of nations declines too” [1]. The importance of protecting good status waters is also emphasized by the Water Framework Directive, as an important aim for Member States and candidate countries in their approach to improving water quality [2]. The fate of heavy metals and other chemicals introduced by human activities, chemical and geochemical processes into the aquatic ecosystem has recently become subject of widespread concern; since beyond the tolerable limits they may become very toxic [3].

Mediterranean Region looks sensitive toward impacts of climate change and its continuous sustainable economic and social development is highly dependent on clean, fresh water resources. The main characteristic of rivers is their continuous one-way flow in response to gravity. Although moving water dilutes and decomposes pollutants more rapidly than standing waters, their quality is greatly influenced by urban, industrial and agricultural activities, which are mainly concentrated along rivers. Their traditional use as recipients of effluent has had obvious negative environmental impacts.

The hydrographical basin of Albania has a total area of 43,305 km², where 28 500 km² from which only 65% are situated within the Albanian territory [4]. Around 98 % of energy production comes from hydropower plants, while agriculture is fully dependent on irrigation. The mining and industrial sector, as well as tourism activities, is strongly dependent on clean and sufficient fresh water. It is a known fact that Albania, despite being naturally rich in water (far exceed its use), suffers from a lack of fresh water in the required quantity and quality [5]. In this condition, the responsibility to protect and use properly the water resources is imperative, because the present state of water pollution in

Albania is a real risk for the economy and human health [6].

Erzeni River

Erzeni is one of Albania's main rivers. It is 109 km long and its tributaries form a water catchment of 760km². This river originates from the Eastern Tirana Mountains and flows to the Adriatic Sea, north of Durrës. The average flow rate is 18.1 m³s⁻¹, varying from 35m³s⁻¹ at the begin of the year to nearly 4m³s⁻¹ after the dry summer period [7], [8]. River watershed is field-mountainous with mean altitude of 435 m above sea level. The average annual amount of precipitation increases toward the upper zone, from about 900 mm per year in over 1600 mm. The waters of Erzeni River have low mineralization of bicarbonate-calcium type, in average 300-350mg/l. [9].

Conventionally, Erzeni River is usually classified together with the Ishmi River into a unique basin, which is one of the six main river catchments in Albania. Ishmi-Erzeni watershed is one of the most populated areas in Albania (around 1 million people) containing also extensive agriculture and forested lands. Improper urban and industrial solid waste management, the discharge of untreated wastewaters into the rivers, the extensive exploitation of riverbeds for gravel extraction, are some of the main factors that have negatively affected the water quality of Ishmi and Erzeni Rivers. Several studies and monitoring activities undertaken on quality of Albanian Rivers indicate that Erzeni River has a better water quality compared with Ishmi River, which appears to be seriously contaminated and have evidenced it as one the most polluted rivers of Albania. [10], [11], [12], [13], [14].

Even for Erzeni River, the data already available indicate a noticeable change in the physical-chemical and microbiological quality of water along the river: on the upper flow, the river water has a good and sustainable quality because of the lack of human activities, while in the downstream are noticed the increased values of chemical and

microbiological indicators, mainly related with discharge of untreated rural wastewaters [12], [13], [14], [15], [16].

Within the Erzeni River catchment there are numerous and variable diffuse sources. The major sources of diffuse pollution are domestic wastewater from households, restaurants, food processing units not connected with sewer system and agriculture. The majority of food processing industry is made up of small dairies, wineries, oil mills etc., which in most cases lack adequate facilities and practices for treatment and utilization of waste. The treatment of wastewater and residues from production is mostly not in accordance with EU standards. Another source of pollution is illegal trash dumps and scattering of solid waste, especially the plastic, cans and glass bottles. Re-suspension of scattered plastics and other pollutants is observed in flooding cases. Concerning the agriculture as a pollution source, compared to 1980 the use of macronutrient in agriculture is smaller due to reduction of cultivated area. However, recently, the cultivated area is increased, especially towards downstream flow.

The aim of this work is to assess the impact of the increasing economic activities in one region of Erzeni River to the river water quality. Physical-chemical parameters from a river segment of nearly 20 km, have been monitored for several months and the evaluation of the overall water quality has been carried out. The rivers segment chosen for this study includes less populated areas at the upper stream

of river as a reference, and areas with intensive economic, agricultural and human activities as well.

MATERIALS AND METHODS

The water samples have been collected in the river segment from Ibë to Sharrë, between November 2013 and April 2014. A detailed description of sampling stations is given in Tab.1 and their location is presented in Fig.1. Samples have been collected using polythene bottles at about 20 cm under the water surface. Temperature, pH, conductivity and dissolved oxygen (DO) are measured *in-situ*, using portable instrument Multimeter WTW-3420. The collected water samples were transported to the laboratory within the same day, using cooling boxes and were immediately filtered before analysis. Total suspended solids (TSS) are determined after filtering with 0.45µm glass membrane filter, whilst the nutrients are determined by UV-VIS spectrophotometry technique, according to the corresponding (EN) ISO Standards. Aqualytic OxiDirect AL606 BOD-system has been used for BOD₅ measurements. For the COD measurements Aqualytic Check it Direct COD VAR10 photometer has been used. All measurements are performed in duplicate and synthetic control samples are used for quality control assurance.

Table 1. Description of sampling stations

Sampling stations	Description
S1	Ibë: Upstream of Erzeni River, considered as reference point. No apparent pollution source, minor urbanization and other activities.
S2	Peshkatari Bridge: a considerable number of restaurants and hotels (at least 11 known) are situated by the river and develop their activities. In this area there are also many small farms/ houses and an olive oil factory.
S3	Domje Bridge: the extraction of gravels has been evident in several points (at least 3 nearby the bridge and 3-4 non-permanent points in the surrounding area)
S4	Sharra: close to Sharra landfill and the leakages from landfill mixes with river water. Several economic activities are established in the surrounding area, including wood and aluminum processing, as well as a slaughterhouse, which is situated right after the sampling station.

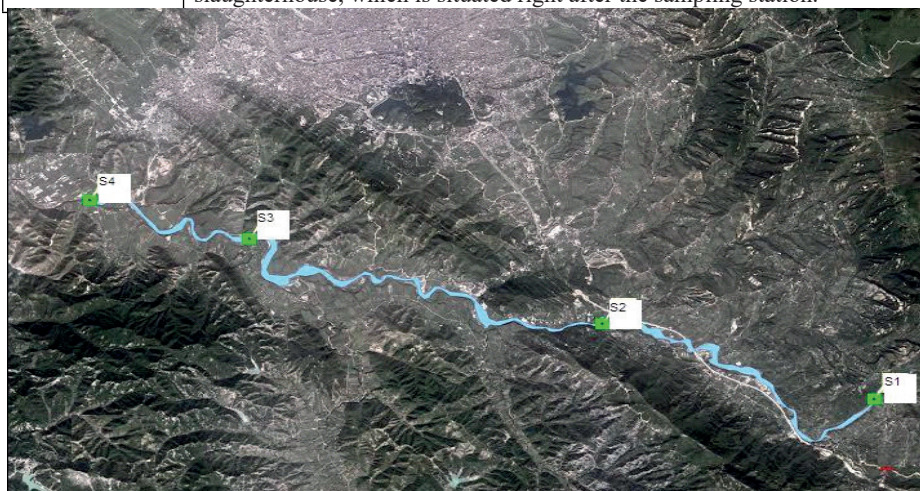


Figure 1. Map of sampling stations

The statistical summary data of assessed physicochemical parameters alongside the river segment are presented in Table 2, whilst figures 2-15 illustrates the variation of monitored parameters by sampling stations.

Table 2. Statistical summary of physicochemical parameters of Erzeni River

Parameter	Mean	Min	Max	St. Dev	Median
Temp (°C) n=26	9.48	5.2	17.5	3.81	8.3
DO(%) n=22	105.3	100.6	125.7	5.54	103.05
DO(mg/l) n=26	11.85	10.28	14.03	1.08	11.95
EC (µS/cm) n=26	438.96	389.00	509.00	38.08	436.00
pH n=26	8.40	8.26	8.67	0.09	8.39
TSS (mg/l) n=16	30.10	3.80	76.60	25.98	18.40
Alkalinity (mg/l) n=24	236.76	207.40	277.55	18.71	234.73
Hardness (°d) n=24	12.21	7.73	14.60	1.34	12.21
NH ₄ ⁺ -N (mg/l)	0.12	<0.08	0.33	0.11	0.04
NO ₂ -N (mg/l) n=26	0.009	<0.007	0.031	0.0077	0.004
NO ₃ -N (mg/l) n=16	0.49	<0.39	0.67	0.13	0.50
PO ₄ -P (mg/l) n=26	0.12	<0.04	0.80	0.20	0.04
Ptot(mg/l) n=26	0.13	<0.06	0.85	0.22	0.04
COD n=20	7.13	n.d.*	18	4.92	7.0
BOD n=20	2.15	n.d.*	7.00	1.81	1.50

*Non detectable

Temperature

Temperature is a significant parameter for a river system, affecting photosynthesis process of aquatic plants, but also the solubility of salts, content of DO, biodegradation of organic compounds and other physico-chemical parameters. The measured temperatures range from 5.2°C to 17.5°C. The mean values of temperature show a slight increase from the first station to the fourth one (Fig. 2), therefore can be serve as an indicator for urban and/or industrial effluent discharges. The minimum temperature values are almost the same in the four stations, while the highest value of temperature is measured in station S4.

pH-value

The mean pH values remain practically constant between sampling stations 1-4 (Fig.3), ranging from 8.26 to 8.67. These values show an alkaline nature of the river water, which can be explained by the presence of limestone rocks in the area. The measured pH values are within the range which is considered suitable for fisheries (5.0-9.0), though 6.5-8.5 is preferable [17]. A slight increase of pH value is observed alongside the river, going from S1 to S4. Such minor increase of pH might be due to ammonia contribution, which may derive from untreated discharge of domestic waters and other activities. The level of HCO₃⁻ ranges from 207.4 to 277.6 mg/l, which corresponds with the results of previous studies [9]. The mean levels of HCO₃⁻ gradually increased from station S1 to S4 (fig.4), and the same trend

is observed also for hardness and conductivity (fig. 5 and 6).

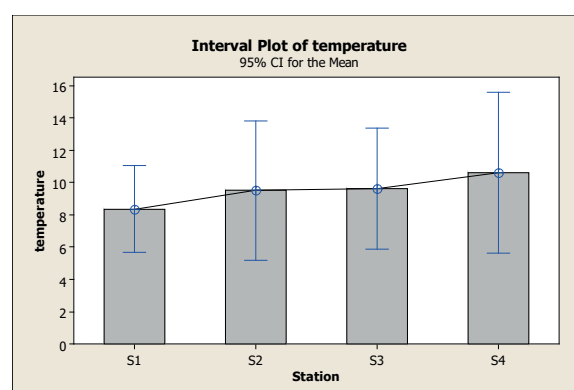


Figure 2. Variation of water temperature by station

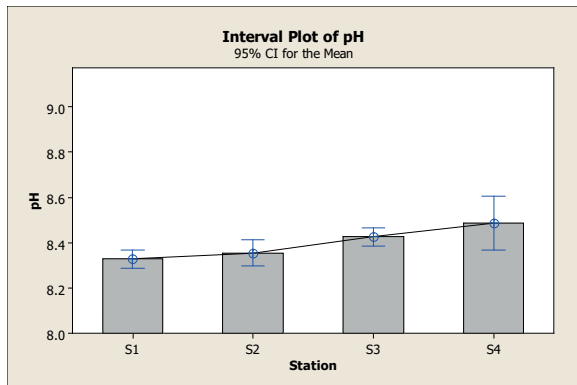


Figure 3. Variation of water pH by stations

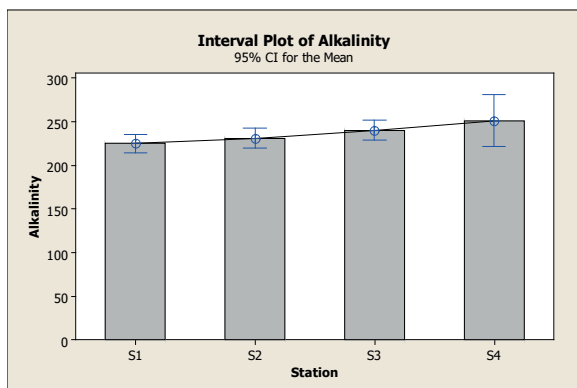


Figure 4. Variation of water alkalinity by stations

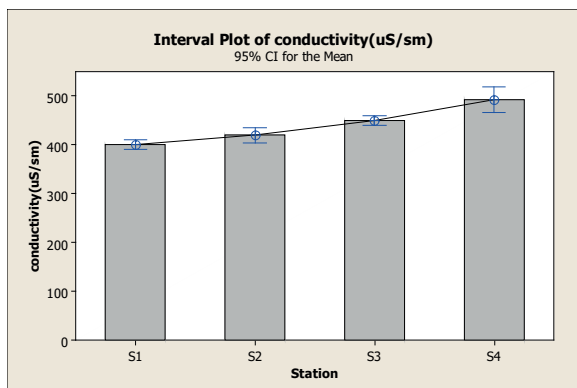


Figure 5. Variation of water conductivity by stations

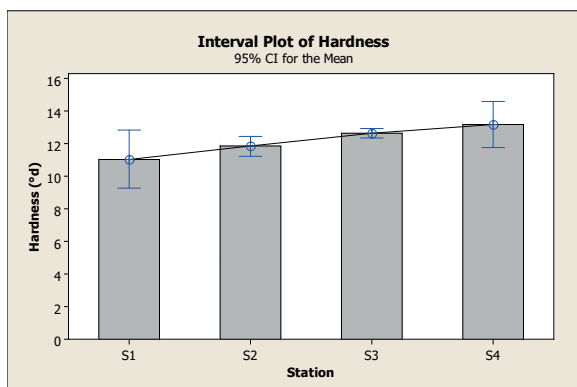


Figure 6. Variation of water hardness by stations

Dissolved Oxygen

The dissolved oxygen (DO) concentration in rivers is one of the most important quality-defining factors, since it determines the flora and fauna living in water. On the other hand, it is also a precondition for the concentrations of other numerous chemical species, e.g. the ratio of ammonia, nitrate and nitrite [18]. The DO concentration correlates to water temperature and partial pressure of oxygen in the atmosphere. Since the solubility of oxygen in water at 25°C is 8.32 mg/L, the values observed seem to be closed with equilibrium values calculated by Henry’s Law [18] at all four stations (fig. 7). It looks that almost no oxygen-consuming processes are occurring in the water layers, between S1 and S4. Comparing the means by *t*-test, it was found that there is no evidence that sampling site can affect the amount of oxygen dissolved. No significant difference was found between mean values. Thus, the values of DO show that the water quality is not affected significantly by the anthropogenic activities in the studied river segment.

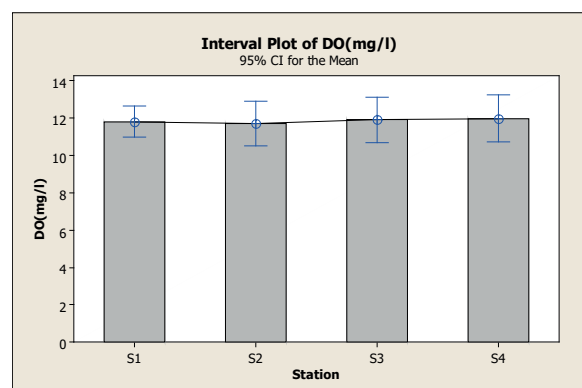


Figure 6. Variation of dissolved oxygen by stations

Total Suspended Solids

TSS is a useful parameter as it provides an actual weight of the particulate material present in the sample. The trend of TSS increasing is quite obvious whilst going from station 1 to station 4 (fig 7). Such increase is due to solids present in sanitary wastewater and many other discharging wastewater activities. Systems for the collection of municipal solid waste (MSW) are provided in most cities and towns, but not in rural areas. Urban waste is mostly disposed of at designated landfill sites, but large quantities are also dumped at unauthorised locations at the edges of settlements and along roads and rivers. The pollution from solid particles in Erzeni River is worsen also by presence of numerous gravel extraction plants located along the river banks, which discharge the used waters from the washing process directly to the river.

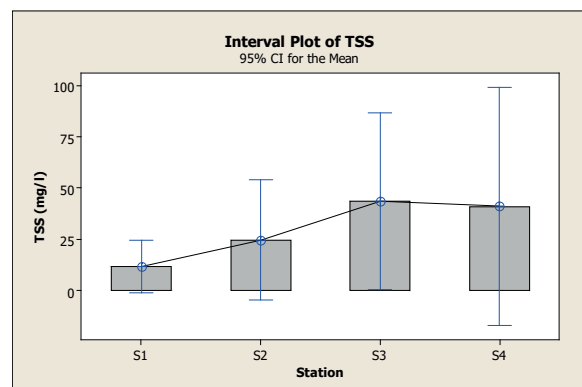


Figure 7. Variation of TSS by stations

When a TSS concentration of less than 25 mg/l has been measured, a clear appearance of water has been observed in the sampling sites, but when the concentration of TSS was higher than 50 mg/l the water appeared cloudy. From our experience when the concentration of TSS is higher than 150-200 mg/l, the water appears dirty. However, in all our stations, the water samples have shown values lower than 80 mg/L. The nature of the particles that comprise the suspended solids may have caused these numbers to vary. The TSS values found in the first station have not exceeded 18 mg/l. In that station TSS even reached the minimum value of 3.8 mg/L, indicating that in the upper stream the river is rather transparent.

The highest TSS values have been observed at stations 3 and 4. At station 3 the encountered values changed in a wide range (10.2 to 76.6 mg/L), depending whether or not gravels have been extracted from the river bed in time of sampling. At this part of the river, inappropriate exploitation has caused a significant erosion of the river banks. While, station 4 is localized near Sharra landfill (landfill of Tirana City), therefore is naturally expected to have higher values of TSS.

The river banks in areas nearby sampling sites are generally covered with vegetation, thus natural inputs of the TSS values should be small. However, human factor and all related activities have influenced and significantly increased the TSS values when passing from S1 to S4.

Nutrients concentration

The nutrients into the rivers originate mainly from agriculture and domestic sewage. It is estimated that agriculture is the largest contributor of nitrogen pollution, and contributes with half of the total phosphorus load to European waters [19]. The release of nutrient into water bodies stimulates the growth of phytoplankton and other aquatic plants, causing the eutrophication of vulnerable water bodies. Such nutrient enrichment can cause significant changes in the balance of aquatic ecology. The eutrophication is more apparent in lakes, reservoirs and large low flowing rivers, than in small rivers [20].

Ammonium, nitrite and nitrate concentrations showed the same trend, increasing from stations S1 and S2, to stations S3 and S4 (figures 8-10). Applying *t*-test, a significant difference between the ammonium mean value of station 4 with the mean values of stations 1, 2 and 3 has been found (the probability associated with student's *t*-test resulted lower than 0.05). No significant differences have been observed for the mean concentrations of ammonia between stations 1, 2 and 3. The sampling station S1 is considered a reference station (located in the upper stream), however the first three sampling sites seem not polluted by ammonium. The conclusion is that along the first three stations area, where the population is quite small, no pollution is observed. The values increased significantly at station 4, which seems to receive part of not treated wastewaters. Moreover, it is located nearby a landfill. However, it seems that most of the wastewaters of the city of Tirana are discharged in Ishëm River and its ramifications. Comparing the values of ammonium it looks that in the monitored section, for stations 1 and 2, the quality is almost of Salmonid waters (< 0.04 mg/L), whereas for stations 3 and 4 is of Cyprinid quality waters (0.2 to 1.0 mg/L) [21].

In regard to nitrite, a significant difference is found between the mean values of station 4 with stations 1 and 2. While, no significant difference is found between mean concentrations of stations 4 and 3 (the probability associated with student's *t*-test for stations 4 and 3 resulted 0.768). It looks that the concentrations of both NO_2^- and NO_3^- start increasing due to pollution through discharge of wastewater from urban settlements and from small industrial activities, which at stations 3 and 4 are increased. We point out that

most rural areas have individual household wastewater collection systems with no drainage pipes. In addition, all industrial activities located nearby the river, discharge wastewater directly without pre-treatment. However, nitrate concentrations in all analyzed samples are much lower than the EC Guide value of 25 mg/L, for surface waters [22]. The nitrite concentrations for all analyzed samples (except one in station 4) are below the 0.03 mg/L, which is the EC Guide value for Cyprinid waters. Whereas, for sampling stations 1 and 2, the water quality is of Salmonid waters (< 0.01 mg/L)[21]. The low concentration of NH_4^+ and NO_2^- is in concordance with high concentration of dissolved oxygen. However, the concentration of NO_3^- is still low.

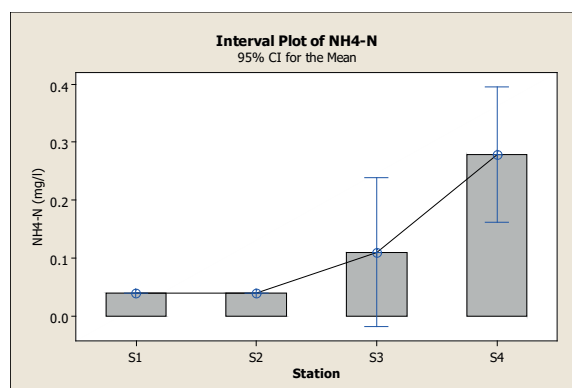


Figure 8. Variation of ammonium concentration by stations

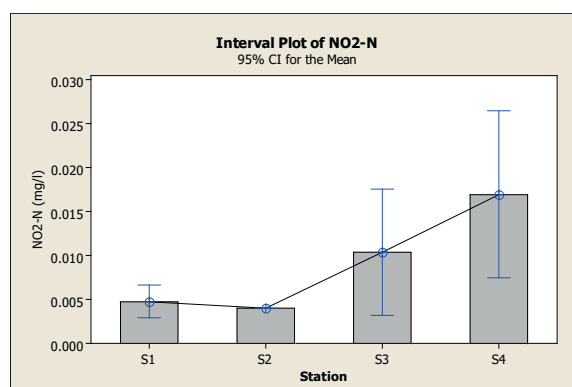


Figure 9. Variation of nitrite concentration by stations

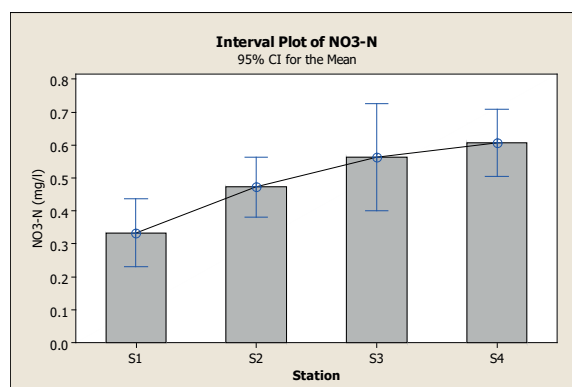


Figure 10. Variation of nitrate concentration by stations

Phosphorus is an important nutrient for plant growth. Increased phosphorus concentration leads to the eutrophication of the aquatic environment. Phosphorus originates from a variety of sources, many of which are related to human activities. Major sources include human

and animal wastes, detergents and agricultural runoff. Phosphorus is measured in two ways, as ortho-phosphate (soluble reactive phosphorus) and total phosphorus and their spatial variation are illustrated in figures 11 and 12. The calculated ratio of PO_4^{3-} / P_{tot} of 90% indicates that most of the phosphorus is dissolved and is easily available for plants. The highest values of phosphorus were recorded on 27 November 2013 when the average concentrations of all stations were 0.57 mg/l and 0.60 mg/l respectively for phosphates and total phosphorus. Such results may be explained by the weather conditions; although, the sampling day was not a rainy one, the river water was too turbulent, unclear and muddy, as a consequence of continuous rainfalls in the previous days. In other sampling days, the levels of phosphorus are significantly lower and vary from 0.02 to 0.077 mg/l, recording highest concentrations at stations 3 and 4. But taking into account that the phosphorus concentration greater than $50\mu\text{g/l}$ are attributed to human activities [20] it may be concluded that in two last stations the influence of humans activities have contributed in increasing of phosphorus levels in river water.

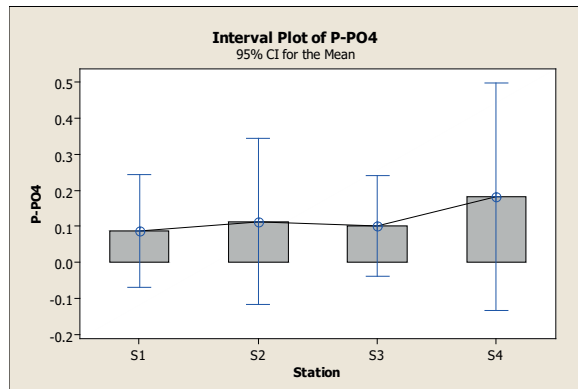


Figure 11. Variation of phosphate concentration by stations

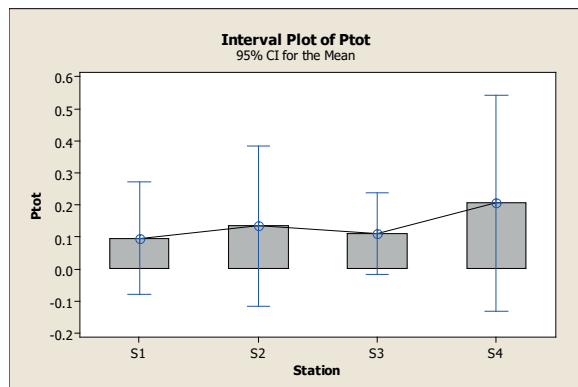


Figure 12. Variation of total phosphor concentration by stations

Organic pollution

The most important sources of organic pollution into rivers are domestic and industrial sewage. Because decomposition of organic matter requires oxygen, the amount of organic matter in river can be measured in terms of oxygen demand (biochemical oxygen demand BOD and chemical oxygen demand COD). River which are little affected by human activities have a BOD below 2mg/l O_2 , whereas a BOD exceeding 5mg/l O_2 , indicates pollution [20].

The data for COD showed relatively low values for stations S1 and S2 (up to 9mg/l O_2), while almost doubled

for stations S3 and S4 (up to 18mg/l O_2). (fig. 13). The same situation encountered for BOD. (fig.14). The low levels measured of COD and BOD, below or close to LOQ values do not allow a statistical interpretation of the results regarding to variation of these parameters between the four sampling stations.

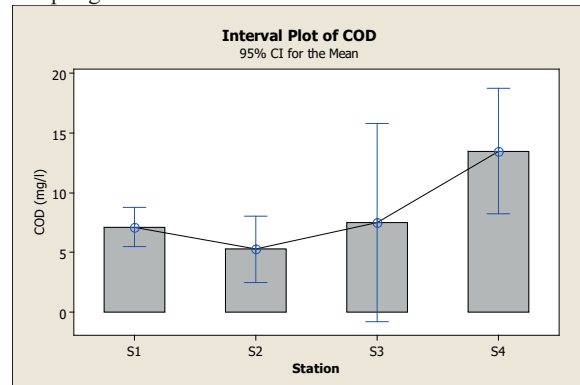


Figure 13. Variation of COD by stations

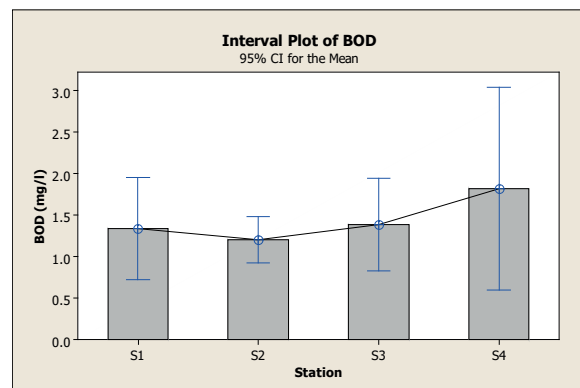


Figure 13. Variation of BOD₅ by stations

Water Quality Index (WQI)

WQI relates a group of water quality determinants to common scale and combines them into a single number, in accordance with a chosen method or model of computation. The use of WQI is a simple practice which allows adequate classification of water quality

For calculation of water quality index following empirical equation has been used:

where k is a subjective constant with a maximum value of 1 for apparently good quality water and 0.5 for apparently highly polluted water, C_i is the value assigned to parameter i after normalization and P_i is the weight of the parameter. In order to avoid the subjectivity in evaluation of k , the constant has not been considered [23]. Calculated WQI values vary from zero (highly contaminated water) to 100 (excellent quality water) percent (table 4).

Table 4 Classification of water quality according WQI values [24]

Range	Quality
0-25	Very bad
25-50	Bad
51-70	Medium
71-90	Good
91-100	Excellent

WQI was calculated for four sampling stations based on average values of eleven physical-chemical parameters: pH, temperature, conductivity, dissolved oxygen (DO), total

suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD₅), ammonium, nitrite, nitrate and total phosphorus. Based on the calculated WQI values, a classification of water quality has been carried out for each station and is presented in figure 15.

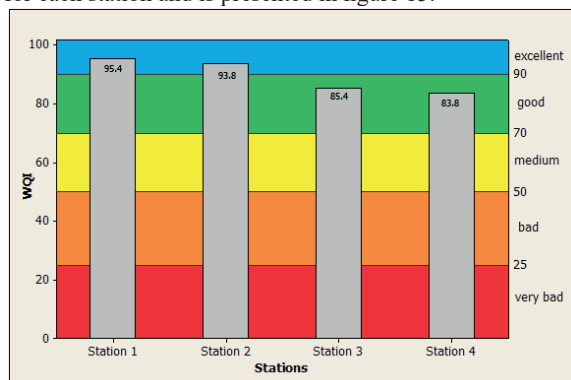


Figure 15. Classification of the stations according WQI

The greater WQI values, which indicate a very good water quality, correspond to the stations S1 and S2. For both stations, situated in the upper stream of Erzeni River, the water could be classified as excellent and this can be explained by the limited human activities on the surrounding areas. At stations S3 and S4, the WQI values are 85.4 and 83.8 respectively, therefore the waters could be classified of a good quality. While going downstream of the river, a continuous decrease in WQI values can be observed, which confirms the decline of water quality, due to the discharge of various domestic and industrial wastewaters, and also other anthropogenic pollutants along the rivers stretch.

CONCLUSIONS

- Through the proper selection of four sampling stations in a river segment of nearly 20km and monitoring of proper chemical water parameters for a period of half a year, the alteration of water quality downstream the Erzeni River (from S1 to S4) has been observed.
- The statistical assessment of the physical-chemical parameters measured and the use of the described WQI-Methodology clearly demonstrated the deterioration of water quality in the investigated river segment. The water quality in this river sector changed from “excellent” to “good” one and this is a consequence of the economic activities in the region.
- This approach can be used for further monitoring studies regarding water quality of rivers or river segments, which are especially under pressure from anthropogenic activities and economic developments in the region. The estimation of biological characteristics alongside with the above mentioned approach is strongly recommended for further studies.

Acknowledgments: This work is performed under the project “Assessment of the water quality of Erzeni River in Albania and the impact of economic developments therein”, Ref. No. 1206.002A-13, financed by the Central European Initiative (CEI) with funding of the Austrian Development Cooperation (ADC).

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