# THE EFFECTS OF INDUSTRIAL AND AGRICULTURAL ACTIVITY ON THE WATER QUALITY OF THE SITNICA RIVER (KOSOVO)

# UTJECAJ INDUSTRIJE I POLJOPRIVREDE NA KVALITETU VODE RIJEKE SITNICE (KOSOVO)

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An important issue in Kosovo is water pollution. The use of polluted water has a direct impact on human health and cause long-term consequences. The longest and most polluted river in Kosovo is the Sitnica, a 90 km long river with its source located near the village of Sazli. The river flows into the Ibar River in Northern Kosovo. Agriculture is prevailing activity in the basin of Sitnica which is why agricultural as well as industrial waste are the biggest water pollutants. The purpose of this study was to evaluate water quality of the river and analyse the pollution level along the Sitnica River caused by agricultural activities and industrial discharges. In order to assess the impact of pollutants on this river, a measurements were carried out in four (five) monitoring stations: the first station represents the reference station which has not undergone or has not been affected by polluting pressures, two stations in water areas affected by the irrigation of farming land and two monitoring stations in water areas affected by industrial wastewater discharge. Some of the parameters of water quality analysed are temperature, turbidity, electrical conductivity, pH, DO, COD, BOD, P total, nitrates, sulfates, and heavy metals iron, manganese, zinc, nickel. Compared to the reference station the results obtained from the Gracka and Pestova monitoring stations prove that the dominant form of pollution is that from agricultural lands irrigation, while the Plemetin and Mitrovica stations show that the Sitnica River is affected by wastewater discharge which contains significant concentrations of heavy metals, as well as metal ions selected in this paper. It can be concluded that the irrigation of agricultural lands and discharges from mining significantly affect water quality of the Sitnica River.

**Keywords:** Water pollution, water quality, land use, Sitnica River, Kosovo

Onečišćenje voda predstavlja veliki problem u Kosovu. Uporaba onečišćene vode ima izravan utjecaj na ljudsko zdravlje te može imati dugotrajne posljedice. Najduža i najonečišćenija rijeka u Kosovu je Sitnica, 90 km duga rijeka čiji se izvor nalazi u blizini sela Sazli, a ulijeva se u rijeku Ibar u sjevernom Kosovu. Poljoprivreda je najzastupljenija djelatnost u slivu Sitnice zbog čega poljoprivredni, ali i industrijski otpad predstavljaju najveće onečišćivače voda. Cilj ovog istraživanja je ocijeniti kvalitetu vode rijeke i analizirati razinu onečišćenja duž rijeke Sitnice koja je posljedica poljoprivredne djelatnosti i industrijskog onečišćenja. Da bi se ocijenio učinak onečišćivča, provedena su mjerenja u četiri (pet) mjerne stanice. Prva stanica predstavlja referentnu stanicu koja nije bila pod izravnim ili neizravnim utjecajem tereta onečišćenja, dvije stanice u području rijeke zahvaćene su navodnjavanjem poljoprivrednog zemljišta, a druge dvije u području rijeke zahvaćene su ispuštanjem industrijskih otpadnih voda. Neki od analiziranih parametara kvalitete vode su temperatura, zamućenost, električna provodljivost, pH, DO, COD, BOD, ukupni P, nitrati, sulfati i teški metali željezo, mangan, cink i nikal. U usporedbi s referentnom stanicom rezultati dobiveni u mjernim stanicama Gracka i Pestova dokazuju da prevladava onečišćenje koje dolazi od navodnjavanja poljoprivrednog zemljišta, dok stanice Plemetin i Mitrova pokazuju da je rijeka Sitnica izložena ispuštanju otpadnih voda koje sadrže značajne koncentracije teških metala kao i metalnih iona odabranih u ovom radu. Može se zaključiti da navodnjavanje poljoprivrednog zemljišta i ispuštanje otpadnih voda rudarstva značajno smanjuju kvalitetu vode rijeke Sitnice.

**Ključne riječi:** onečišćenje vode, kvaliteta vode, uporaba zemljišta, rijeka Sitnica, Kosovo

## Introduction

Water is one of life's basic needs. With an increasing population, the need for water has increased, too. However, pollution reduces the amount of water available for use. Water is assumed to be polluted when there are changes in its quality that constitute a threat to living organisms or make it unusable because of its physical, chemical and biological changes (Manastirliu, 2013). Water pollution is a threat to ecosystem itself and also to the health of people. This is a problem of a great importance and calls for solution especially considering the developing countries, where practices of environmental administration stay behind the economic development (Agusto, Bamigbola, 2007; Bushati, 2013).

Increasingly, the urban way of life, industrialization, modern agriculture and agricultural technology is using an ever-greater number of major raw materials and agents. After their use in various production processes, they pollute the environment through their preliminary inflow in water streams (rivers) or large masses of water (lakes and seas). Contemporary water pollution is mainly associated with various industrial processes, in which case large amounts of water are used (Rozhaja, Jablanoviq, 1983).

In addition to industrial wastewater, waters are being polluted from the use of agricultural preparations (pesticides) in agricultural lands. If these polluted waters are not treated before being discharged into the environment, they present a risk to the flora and fauna that live in those waters. A very dangerous effect is caused due to the increase of "necessary biological oxygen" in these environments (Korça, 2003).

Although water is a renewable source, abuse and mismanagement of the water system can cause problems in the quality and provision of drinking water. Water can get polluted in many ways, for example chemically and biologically and may become unclean for drinking and cannot be used for other purposes (Raja et al., 2008). Rivers and their flows are of heterogeneous composition in the spatial aspect and also in the aspect of the importance they have regarding earth; therefore many scientists have documented this heterogeneity focusing on the physical-chemical dynamics of the rivers (Singh et al., 2010).

Therefore, one of the most important and at same time contaminated resourses not only in Kosovo, but in other countries, too is water, without which life would be impossible. Based on research available the Sitnica River, starting from Ferizaj to Mitrovica, is the most polluted river in Kosovo. Suspensions are present in it and exceed the maximal allowed values (main findings are given by the Authority for Surface Waters Quality, MESP, the Ministry of Environment and Spatial Planning, Department of Water, see Morina, 2014).

Historically, the Sitnica River has been surrounded by many residential areas and has been an important factor of regional development. Until recently, this river's water was an important source for the neighbouring settlements and was used for different purposes, such as water supply, irrigation, fishing, and recreation. In recent times, the Sitnica River has been converted into a natural recipient of wastewaters, like those coming from Kosovo power plants in Obiliq, waters from bigger and smaller central urban sewage systems and those which have increased the contamination of the water due to waste water discharges (Arbneshi, 2008).

The flow of the Sitnica is subjoined by small rivers like Graçanka, Drenica, Llapi and Prishtevka, which are also recipients of wastewaters of different urban and industrial centres (Korça et al., 2002). The Sitnica River passes through a large number of cities in Kosovo (Fig. 1) that still have no wastewater treatment plants and sewage what so ever. Industrial and agricultural wastewaters are deposited directly into the river. These processes have contributed to a considerable increase of this river's pollution. The non-management of wastewater discharge of urban residential areas, industrial discharges, the use of pesticides and insecticides in agriculture, livestock excrement and lack of proper treatment and reuse of waste led to a reduced quality of surface water bodies, but also of the earth surface itself (Faeth, 2000; Gundogdu, Guney, 2007; Bode, 2012).

In this sense, the assessment of surface water quality and determining the main pollutants discharged therein are important. The final goal is the protection and/or rehabilitation of the environment and creation of a database for integral and sustainable management of water resources (Kuchment, 2003; Bode, 2012). To achieve the research objectives, water samples were taken at five monitoring stations along the flow of the Sitnica River and physical and chemical parameters and heavy metals have been analysed at the Hydrometeorological Laboratory of Kosovo.

## Materials and methods

The aim of the experimental part of this research was to determine the presence of contaminants caused by anthropogenic activity in the Sitnica River through defining the values of selected parameters for monitoring. The survey was carried out in 2014 in three periods (spring, summer and autumn) in order to see the impact of climate (seasonal) changes while the parameters were analysed in the Laboratory of the Hydro-Meteorological Institute of Kosovo. Sampling was carried out based on standard ISO 5667-6: 2014 which sets out the principles to be applied to the design of sampling programmes, sampling techniques, and the handling of water samples from rivers and streams for physical and chemical assessment (URL 1). To reflect the impact of industrial discharges and agricultural water quality in the Sitnica River, sampling points included three types of aquatic areas, as follows (Fig. 1):

1. water area unaffected by the pressures of anthropogenic pollution (reference station: Devetak).
2. Aquatic areas affected by agricultural wastewater discharges (stations: Gracka and Pestova).
3. Aquatic areas affected by industrial wastewater discharges (stations: Plemetin and Mitrovica).

The first monitoring station Devetak is located in the spring of the Sitnica River, the station Gracka belongs to the upstream, Plemetin station is located in the middle flow while the last two stations Pestova and Mitrovica belong to downstream of the river. Water samples were taken in glass bottle for organic parameters and in polyethylene bottles for inorganic parameters. Sample bottles were labelled including time, date and source of sampling. They were preserved in the refrigerator at 4 °C and transported according to respective procedure. For determination of heavy metals, samples were taken in a polyethylene bottle, and

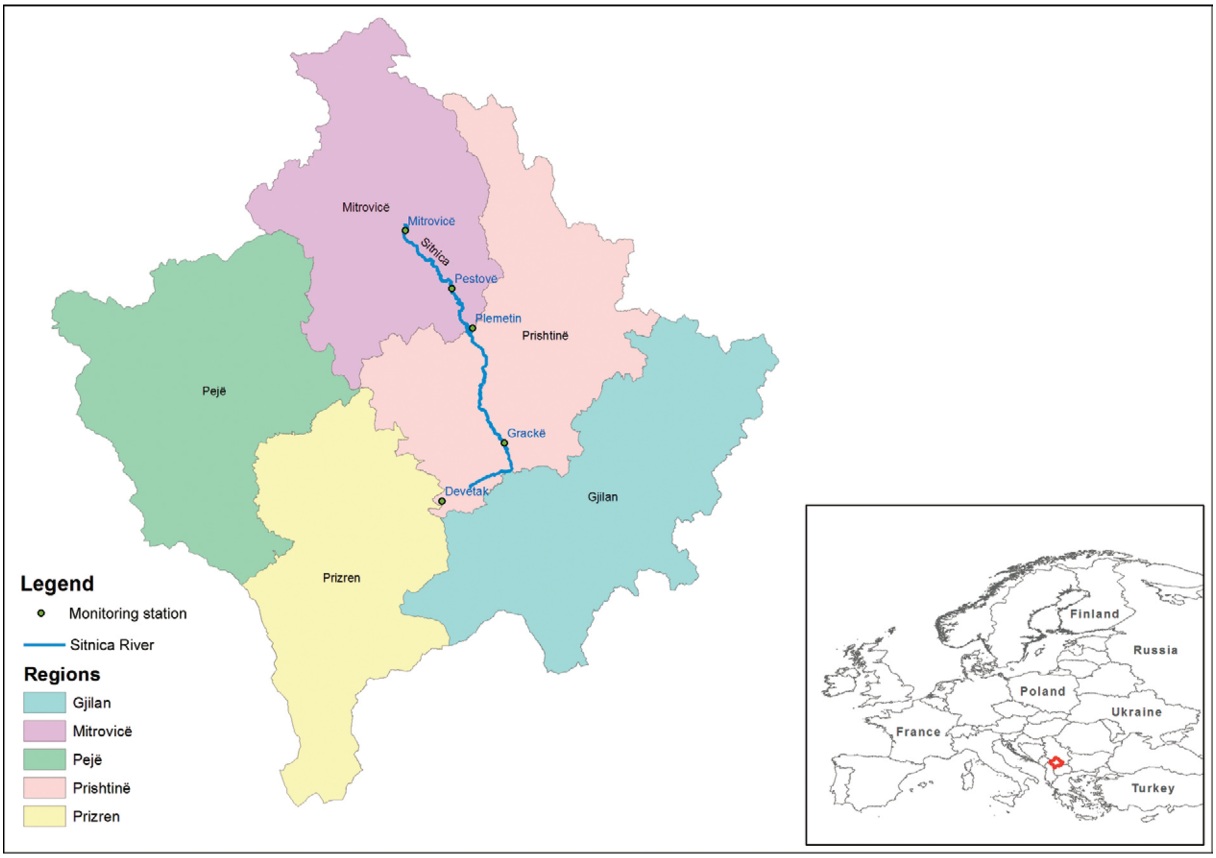


Figure 1 Map of Kosovo and monitoring stations of the Sitnica River

0.5 ml / nitric acid ($HNO_3$) (cc/100ml) sample was added immediately for preservation.

Some of the parameters were measured directly in the ground (mainly physical parameters). At each sampling point, the following parameters were measured: temperature, electrical conductivity, pH, dissolved oxygen, while chemical analyses were carried out in the analytical laboratory of Hydrometeorological Institute of Kosovo.

Analysis of physical and chemical parameters of water samples taken from the Sitnica River was conducted using the following tools: Multi 340i thermometer – used to measure temperature; turbidity was measured with Turbid meter AQUALITIC / PC COMPACT – ISO 7027 (photometry); electrical conductivity was measured using conduct meter WTW 315i; pH values were measured using the HI 98130 pH meter (DIN 38404 – C5); levels of dissolved oxygen were determined by the HI 9146 – ISO 5814 (Electrochemical); BOD – ISO 5815-2 and COD – ISO 15705; P-total – ISO 15681-2, $SO_4^{2-}$ – ISO 15923, $NO_3^-$ – ISO 7890/1 with SECOMAN PRIM-LIGHT UV – VIS Spectrophotometer, while the quantity of certain heavy metals was determined by the atomic absorption spectrophotometer – ISO 8288 (Perkin Elmer type Analyst 400). Calibration and evaluation of analytical methods and estimation of performance characteristics, Part 2: Calibration strategy for non-linear second-order calibration functions – ISO 8466-2.

## Results and discussion

Results for the analysed parameters are presented in Table 1 and 2 with sampling stations are represented by codes, parameters of monitoring, their measuring units, values recorded in three monitoring periods (spring, summer and autumn) for each analysed parameter. The comparison between the three periods is reflected in the diagrams presented in Figures 2 to 11.

Temperature had variations in three monitoring periods. During spring variations were from 6.4 (S1) to 13.2 °C (S3), in summer from 14.9 (S1) to 22.2 °C (S5), whereas in autumn it water temperature varied from 10.2 (S1) to 15.5 °C (S3). The biggest change of temperatures was between seasons of spring and summer reaching about 9.5 °C, while between autumn and summer changes were smaller and reach up to 7 °C. The rising of the temperatures was influenced by air temperatures which increase in summer and especially during midday, in addition to that, urban discharges also contributed to the increase of temperatures.

Table 1 Results of physical and chemical parameters

| Parameters | Units | Station | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Devetak (S1) | | | Gracka (S2) | | | Plemetin (S3) | | | Pestova (S4) | | | Mitrovica (S5) | | |
| | | Sp | Su | A | Sp | Su | A | Sp | Su | A | Sp | Su | A | Sp | Su | A |
| Temperature | °C | 6.4 | 14.9 | 10.2 | 12.7 | 21.2 | 14.7 | 13.2 | 19.9 | 15.5 | 12.4 | 21.6 | 14.6 | 12.6 | 22.2 | 15.0 |
| Turbidity | NTU | 9.5 | 61 | 9.2 | 3.3 | 14.4 | 9.7 | 7.7 | 17.2 | 9.1 | 3.5 | 5.2 | 16.5 | 4.0 | 5.4 | 17.0 |
| Conductivity | μScm-1 | 262 | 280 | 270 | 645 | 560 | 680 | 831 | 660 | 610 | 612 | 680 | 570 | 616 | 640 | 610 |
| pH | 0-14 | 7.99 | 7.85 | 8.20 | 7.75 | 7.25 | 7.514 | 7.80 | 8.27 | 7.58 | 7.78 | 7.66 | 7.76 | 7.76 | 7.48 | 7.56 |
| Dissolved oxygen | mg/L | 10.51 | 7.40 | 9.37 | 5.48 | 1.60 | 3.03 | 0.53 | 2.40 | 2.84 | 4.82 | 1.70 | 3.21 | 6.76 | 3.50 | 4.17 |
| Chemical oxygen demand (COD) | mg/L | 18.0 | 4.2 | nd | 30.0 | 57.0 | 65.5 | 26.4 | 56.0 | 58.2 | 11.3 | 72.5 | 76.9 | 12.8 | 93.0 | 105.4 |
| Bio-chemical oxygen demand (BOD) | mg/L | 8.5 | 1.9 | <0.1 | 17.0 | 34.5 | 22.6 | 13.9 | 31.0 | 24.3 | 5.40 | 29.4 | 32.9 | 5.5 | 43.6 | 42.3 |
| Total phosphor | mg/L | nd | 0.053 | <0.1 | 0.580 | 0.799 | 0.465 | 0.770 | 0.504 | 0.369 | 0.330 | 0.657 | 0.435 | 0.410 | 0.441 | 0.542 |
| Nitrates | mg/L | nd | nd | nd | 4.3 | nd | 0.3 | nd | 2.4 | nd | 6.5 | 5.9 | 6.3 | 6.7 | 9.9 | 11.2 |
| Sulphate ion | mg/L | 9.103 | 39.8 | 18.6 | 27.29 | 26.06 | 39.88 | 98.15 | 70.45 | 92.86 | 40.82 | 72.78 | 59.92 | 54.51 | 70.73 | 72.90 |

Sp – Spring; Su – Summer; A – Autumn; nd – below the threshold of detection of used method

Turbidity was present throughout the course of the three monitoring periods, the highest values were recorded when it had rained shortly before measurements took place, as it happened in the summer season in the sampling point S1 where turbidity reached the value in 61 NTU, while at other stations the turbidity had lower values, because while doing the sampling there was no rain, and turbidity was caused by consecutive polluting pressures, at S3 we have the case of a slight increase by 2.8 NTU which was caused by the Pristina River, known as collector of all wastewaters of the capital Prishtina which permanently has high turbulence (from the data of KHMI – 31 NTU as VMV – 2014).

From the presentation of data on Table 1 and Figure 3, it can be seen that the electrical conductivity at sampling site S1 in three cases was lower (below 300 μScm-1) that leads to the conclusion that water had high purity and was without polluting pressures. From the station S2 and on, we may note an increase of electrical conductivity along the whole river flow down to S3 where the maximum value reached (831 μScm-1), then the EC value starts to decrease as a result of the intervention of other waters thus causing dilution.

In the water samples that we analyzed, the pH figures recorded do not present a high variability, not more than 1 measurement unit. All pH values are noted to be higher than 7, they range from 7.75-7.99 during the spring season, 7.25-8.27 during the summer and 7.54-8.2 in autumn, slightly alkaline and are generally stable in the region of stable values for all seasons.

Our measurements showed that the values of dissolved oxygen in the monitored stations were different. Highest values during the three periods were at S1 station (reference station), whereas the lowest from the performed measurements was 0.53 mg/L in S3 in spring, S2 with 1.6 mg/L in summer and in S4 with 2.84 mg/L in autumn. It is clear from the diagram that at all stations the quantity of DO is very small and especially during the summer season was significantly lower which confirms the impact of temperature on this parameter.

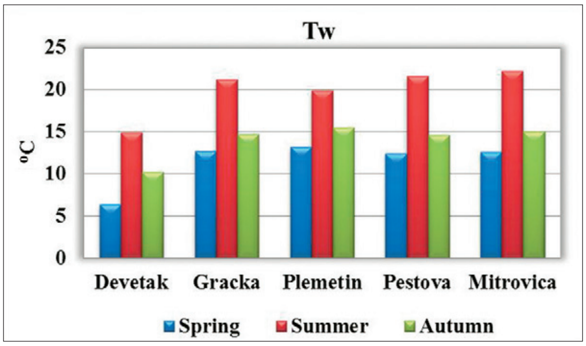


Figure 2 Water temperature according to monitoring stations and seasonal variations

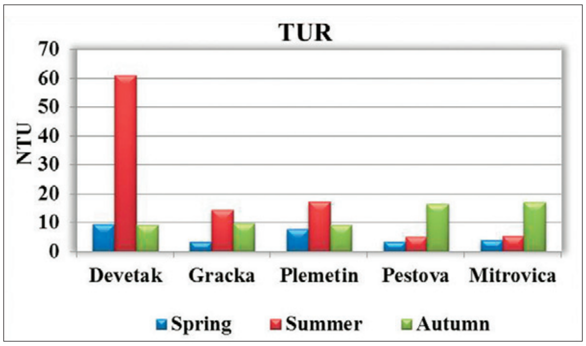


Figure 3 Turbidity for every station and the values by seasonal variation

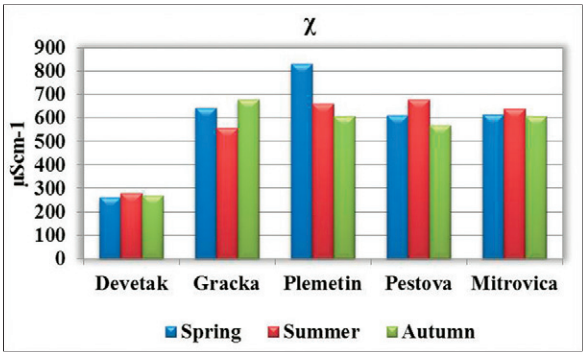


Figure 4 Electrical conductivity according to monitoring stations and seasonal variations

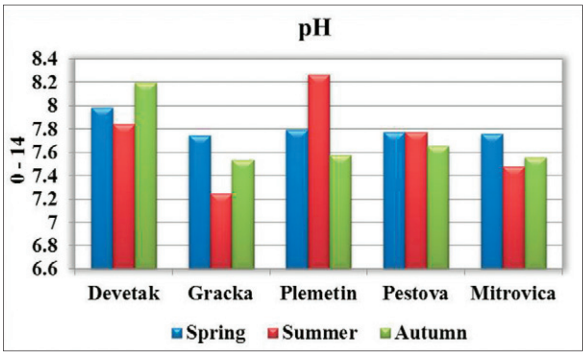


Figure 5 pH according to monitoring stations and seasonal variations

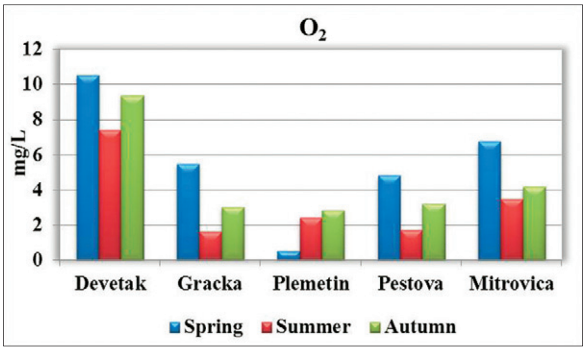


Figure 6 $O_2$ according to monitoring stations and seasonal variations

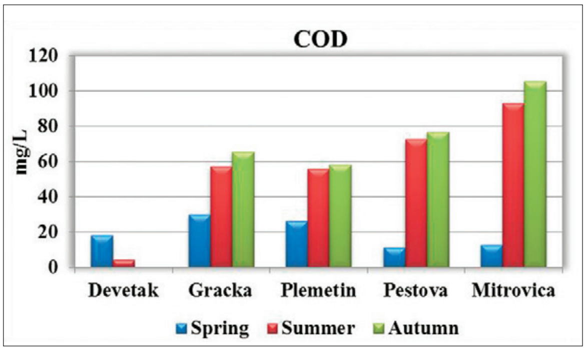


Figure 7 The performance of the values of COD for each station according to seasonal variations

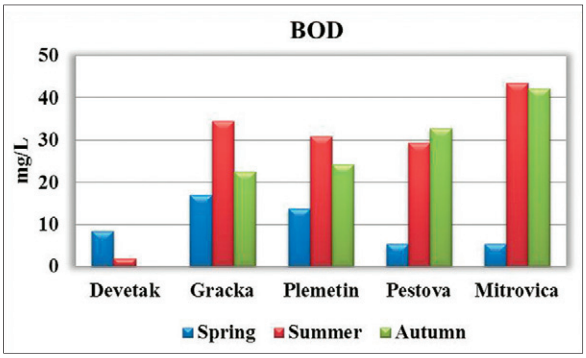


Figure 8 The performance of the values of BOD for each station according to seasonal variations

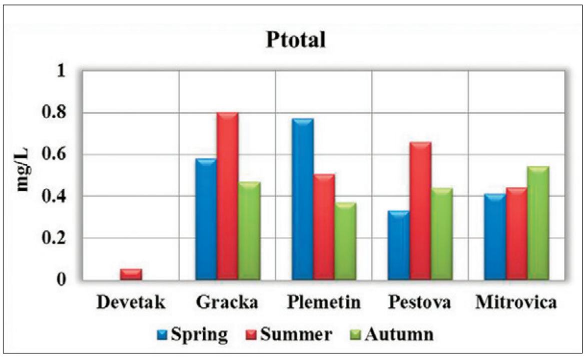


Figure 9 Total phosphorus (mg/l) according to sampling stations and seasonal variations

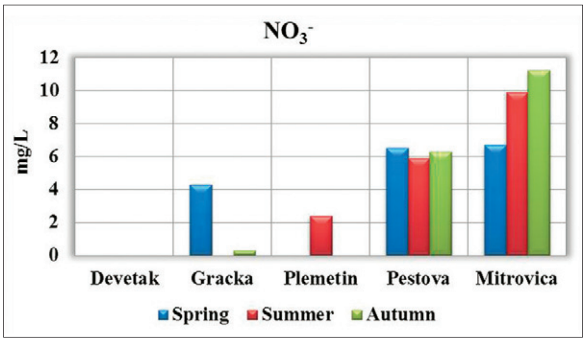


Figure 10 Concentration of nitrates (mg/l) for each station and seasonal variation

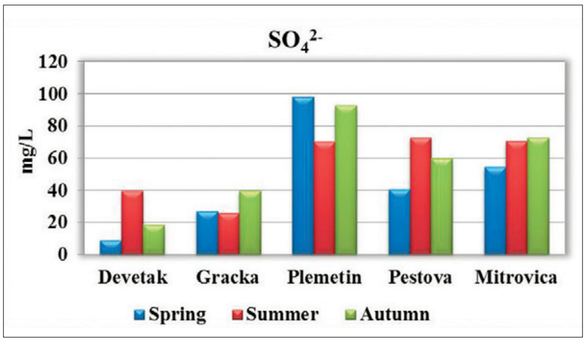


Figure 11 The performance of sulphate ion values according to seasonal variations

Chemical oxygen demand values during the spring vary from 11.3 (S4) to 30.0 (S2) mg/L, in summer from 4.2 (S1) to 93.0 (S5) mg/L, while during autumn they vary from 0.1 (S1) to 105.4 (S5) mg/L. This leads to the conclusion that during all the seasons the Sitnica River is subjected to all pollution types from organic materials in considerable amount where the values are above 100 mg/L.

In the analysed water samples of the Sitnica River, the values of bio–chemical oxygen demand during spring varied from 5.4 (S4) to 17.0 (S2) mg/L, in summer from 1.9 (S1) to 43.6 (S5) mg/L and during monitoring in autumn to 42.3 (S5) mg/L. So it is noted that the quantities were considerably higher during summer and autumn because the river's volume was smaller, while the impact of discharge of water in terms of pollution is higher.

Lowest values of total phosphorus during three periods were recorded in S1, while its highest values were recorded in spring 0.77 mg/L in S3 station, in summer 0.779 (S2) mg/L and in autumn with 0.542 mg/L (S5).

Highest values of nitrates during the three monitoring periods were recorded in the last station, namely S5, in spring with 6.7 mg/L, in summer with 9.9 mg/L and higher in autumn with 11.5 mg/L. The lowest values of nitrates during three periods were recorded in S1 that had values below the threshold of detection of analytical method referred to above. We think that the nitrates in the water of rivers are mainly of urban origin and from agricultural drainage that end in the waters of the river.

Sulphate ions were present in all three stations and during the three monitoring seasons which according to the findings during analysis shows that a smaller quantity was in S1 – 9.103 mg/L and higher quantities in S3 – 98.15 mg/L. This increase comes as a result of the impact from Graqanka River which contains a high quantity of sulphates (KHMI-VMV 300mg/L $SO_4^{2}$) a river which flows into the Sitnica River between stations S2 and S3.

Nickel is one of the metal ions which were detected in all analysed samples. In spring, the level of its concentration was 0.027 mg/L in S1 and its value amounted to 0.055 mg/L in S3 and S5, in the monitoring of the summer season the values varied from 0.013 mg/L in S2 up to 0.026 mg/L in S5 and in the autumn season from 0.017 mg/L in S3 up to 0.033 mg/L in S1. Compared to the EU standards for the allowed values of Ni in surface waters (0.02 mg/L, EU 1998), all the analysed samples taken as a whole during the three seasons have exceeded maximum allowed values.

Values of Zn ions in the samples analysed for this paper, in spring varied from 0.012 mg/L (S1) up to 0.421 mg/L (S5), in summer 0.021 mg/L (S1) up to 3.115 mg/L (S5) and in autumn from 0.042 mg/L (S1) up to 7.772 mg/L (S5) that leads to the conclusion that the Zn ion values in the monitoring station S5 in two seasons, summer and autumn exceeded the values allowed according to the EU standard (3 mg/L, EU 1998).

Mn ions in the samples analysed for this paper had lower values at the station S1, compared by seasons it was noticed that during the summer season the results indicate a higher concentration of Mn. Values ranged from 0.031 (S1) to 0.321 mg/L (S5) in spring, in the summer season from 0.204 (S1) up to 0.550 mg/L (S2) and in autumn from 0.131 (S1) up to 0.214 mg/L (S5). With the exception of the sample of the S1 station of the spring season. Values of Mn are higher than the reference value according to the EU standard (0.05 mg/L).

Iron ions, similarly to ions of other metals, are present all the samples analysed for this paper. If assessing by season, then we may say that in spring these values were from 0.106 (S1) up to 0.369 mg/L (S5), in the summer season it was 0.110 (S5) and at S2 there it was as high as 0.373 mg/L, whereas in autumn the values were from 0.098 (S1) up to 0.446 mg/L (S2). Compared to reference EU standards (0.2 mg/L, EU 1998) the majority were exceeding the allowed values.

Table 2 Concentration of heavy metals

| Monitoring stations | Fe | | | Mn | | | Zn | | | Ni | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sp | Su | A | Sp | Su | A | Sp | Su | A | Sp | Su | A |
| Devetak (S1) | 0.106 | 0.347 | 0.098 | 0.031 | 0.204 | 0.133 | 0.012 | 0.021 | 0.042 | 0.027 | 0.015 | 0.033 |
| Gracka (S2) | 0.322 | 0.373 | 0.446 | 0.223 | 0.550 | 0.169 | <0.01 | <0.01 | <0.01 | 0.040 | 0.013 | 0.026 |
| Plemetin (S3) | 0.290 | 0.161 | 0.229 | 0.282 | 0.495 | 0.159 | <0.01 | 0.028 | 0.033 | 0.055 | 0.021 | 0.021 |
| Pestova (S4) | 0.279 | 0.172 | 0.386 | 0.228 | 0.455 | 0.131 | <0.01 | 0.051 | 0.013 | 0.038 | 0.025 | 0.025 |
| Mitrovica (S5) | 0.369 | 0.110 | 0.414 | 0.321 | 0.450 | 0.214 | 0.421 | 3.115 | 7.772 | 0.055 | 0.026 | 0.026 |
| EU standards 198 (mg/L) | 0.20 | | | 0.05 | | | 3.00 | | | 0.02 | | |

Sp – Spring; Su – Summer; A – Autumn

**Conclusions**

The analysed physical and chemical parameters of the Sitnica River water showed that with the increase of the distance from the source of the river (reference point) to its end (Mitrovica) a deterioration of the water quality is evident. Samples were taken during three periods at 4 monitored stations (Gracka, Plemetin, Pestova and Mitrovica) on the Sitnica River and it can be concluded that the river is very polluted. This confirms the impact of various polluting pressures that come as a result of discharge of waters from a large number of towns and villages that lie on this river and as a result of these impacts, the amount of diluted oxygen is reduced. Results from analyses that were made for determining the amount of heavy metals during three monitoring periods show that their highest concentration was found: in the station S2 for Fe ions in the autumn season, in S2 for Mn ions in the summer season, in S5 for the Zn ions in the summer season and in S2 and S5 for Ni ions in the spring season.

Compared to the EU standards for the allowed values of heavy metals in surface waters, it can be noted that their concentration level in the Sitnica River water was high and exceeded the maximum allowed values. High levels of metal ions content in the Sitnica River water appear as a result of confluence of Graqanka River, where Kizhnica mine waters are pumped into and from the impact of water discharges by Feronickeli corporate in Drenica River which also flows into Sitnica ahead of S3 station, whose waters contain considerable quantities of metal ions (database of KHMI).

Results of this study indicate that given the level of water pollution, measures must be taken as quickly as possible to construct urban and industrial water treatment plants and to apply best and environment friendly practices.

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