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AN ASSESSMENT OF THE WATER QUALITY AND ECOLOGICAL STATUS OF SITNICA RIVER, KOSOVO

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ABSTRACT. The aim of this study is to assess and present the contamination with some environmental toxic parameters of water samples of Sitnica River, Kosovo. Sitnica River is one of the main rivers in Kosovo. The river is located in the area with high anthropogenic pressure, were the contamination of river with different pollutants presents a complex long-term environmental problem. The water samples from Sitnica River were collected from five stations every three months. These stations are covering the upstream and downstream sites of major industrial area of Obiliq city close to Thermo Power Plant (TPP) Kosovo "B" as the main power plant in the country. This Thermo Power Plant apart from air and soil pollution is considered as main source of contamination for the river water as well due to the direct discharged of waste water without any prior treatment. International permissible limits (75/440/EEC) and Kosovo National limits (UA13/2008) were applied to assess the river water contamination. Physico-chemical parameters in water samples from Sitnica River were determined to assess the level of contamination. The concentrations of some toxic parameters such: Fe^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, NO_2^--N, NO_3^--N, NH_3-N, PO_4^{3-}-P were measured using UV-VIS spectrophotometry in accordance with standard method US EPA 6010C.The results showed that the Sitnica River is heavily polluted. The results were summarized using the program Statistica 6.0 descriptive statistical method. In order to protect the river water from further contamination, the remediation options in order to reduce the anthropogenic discharges are suggested.

Keywords: *Physico-chemical, Sitnica River contamination, UV-VIS Spectro-photometry*

INTRODUCTION

There are many ways to define water pollution, and yet most of definitions address towards to excessive concentration of the certain substances which for certain time cause effects than can be hazardous for water ecosystems [1].

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Multidisciplinary collaborative research is essential for understanding the pollution processes. Determination of total quantitative and qualitative metals and distribution of all physical and chemical forms in traces (speciation) in natural water equilibrium resources today is to be considering as the main challenge for most of the scientists. Overexploitation of nature and uncontrolled use of natural resources, including inadequate processing of industrial wastes have caused large contamination of world ecosystems by toxic parameters: Fe^{2+}, Mn^{2+}, Al^{3+}, NO_2^--N, NO_3^--N, NH_3-N, PO_4^{3-}-P.

Due to its position and form, Sitnica River is very interesting for hydro biological studies. It originates as a confluence of two mountain rivers (Shtimanka and Sazlija) and with a total length of 154 km, flows in a South-Northwest direction through the central part of the Kosovo until its confluence into Iber River. This is most important river of the Kosovo walleye and the meeting point for the whole hydrographic network. The catchment area occupies 2861 km2 and is characterized by its high potential or raw materials, favorable geographic position and configuration of terrain, traffic network and concentration of industrial and mining complexes. This river is the sole recipient for a large amount of waste water, which changes its ecological characteristics [2][3].

The aim of this study was the quantitative determination of some environmental toxic parameters in polluted waters discharged from TPP Kosova “B” and the possible impact of these waters on the pollution of River Sitnica as surface water resource. International permissible limits (75/440/EEC) and Kosovo National limits (UA13/2008) were applied to assess the river water contamination. Physico-chemical parameters in water samples from Sitnica Rivers were determined to assess the level of contamination. The concentrations of some toxic parameters: Fe^{2+}, Mn^{2+}, Al^{3+}, NO_2^--N, NO_3^--N, NH_3-N, PO_4^{3-}-P were measured using UV-VIS spectrophotometry in accordance with standard method US EPA 6010C.

The sampling sites in Sitnica River are geographically positioned using Geographic Information System (GIS). The results were elaborated using statistical methods that can be used to locate pollution sources. Selected locations, where certain toxic elements should be monitored and remediation possibly performed, were highlighted [4].

Kosovo as a new country aiming the EU integration has harmonized the national water legislation with EU Water Framework Directive. There are a very few references to waters in Kosovo; however, these are all in respect of the chemical quality [5]. The authors reported the level of contamination in rivers of Kosovo, mainly in water and sediments of Sitnica river, their concentrations were very high due to the inputs of industrial discharge and mining waste erosion. No studies have been reported on the assessment of ecological status of the rivers in Kosovo.

RESULTS AND DISCUSSION

The obtained values are shown in Table 1. From results showed that most of the physico-chemical parameters: water temperature, pH, conductivity, total dissolved solids (TOS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), hardness, concentration of Cl^-, NO_3^--N, NO_2^--N, NH_3-N, PO_4^{3-}-P, SO_4^{2-}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+},Cr^{3+} in water of Sitnica river were found out the permissible limits of both European Legislation 75/440/EEC and Kosovo National Administrative Direction UA 13/2008.

Table 1. Physic-chemical parameters in river water Sitnica

Parameters	A_1	A_2	A_3	A_4	A_5
Water temp./ º C	15.0	16.1	16.5	19.9	15.8
pH/1	11.0	8.41	8.32	10.3	7.64
Conductivity/ μScm^{-1}	475	431	423	459	557
Total dissolved Solids (TDS)/mg/L	18.0	20.4	28.2	37.2	21.2
Chemical oxygen demand (COD)/mg/L	18.0	13.1	15.9	22.1	29.8
Biochemical oxygen demand (BOD) /mg/L	19.3	17.9	20.8	25.2	32.7
Hardness /ºdH	4.07	6.52	8.90	11.2	13.9
Chlorine (Cl^-)/ mg/L	296	55.5	75.5	51.9	97.4
NO_3^--N/mg/L	0.64	1.16	1.32	1.14	1.13
NO_2^--N/ mg/L	0.04	0.10	0.12	0.10	0.21
NH_3-N/ mg/L	0.03	0.04	0.21	0.02	0.50
PO_4^{3-}-P/ mg/L	0.77	0.17	0.57	0.72	0.96
SO_4^{2-}/ mg/L	9.0	28.6	52.7	64.3	62.3
Ca^{2+}/ mg/L	2.57	4.80	5.63	9.32	6.88
Mn^{2+}/mg/L	1.02	0.71	0.51	0.55	0.96
Fe^{2+}/mg/L	2.52	2.96	1.82	1.78	3.10
Al^{3+}/ mg/L	0.89	1.87	2.0	2.04	2.89
Cr^{3+}/mg/L	0.97	1.24	1.32	1.45	2.15

Basic statistical parameters for parameters (mg/L) in five water samples are presented in Table 2. Using experimental data (Table 2) and box plot approach of Tukey [6], anomalous values (extremes and outliers) in waters were determined for the whole region. Frequency distributions of each measured ions and two dimensional scaterplot with plots diagrams are presented in Figure 1 and 2. Anomalous values (outliers and extremes) for 7 variables are presented in Table 3.

Table 2. Basic statistical parameters for nine chemical parameters

Variable mg/L	Mean	Geo. mean	Median	Min.	Max.	Variance	Std.Dev.
Al^{3+}	1.85	1.75	1.87	0.89	2.89	0.53	0.72
Fe^{2+}	2.67	2.62	2.96	1.78	3.10	0.30	0.54
Mn^{2+}	0.75	0.72	0.71	0.53	1.02	0.05	0.22
NO_2—N	0.11	0.10	0.10	0.04	0.21	0.00	0.05
NO_3—N	1.03	1.01	1.13	0.64	1.16	0.04	0.22
NH_3-N	0.27	0.10	0.04	0.02	0.75	0.11	0.33
PO_4^{3-}—P	0.56	0.43	0.72	0.71	0.96	0.13	0.36
Cr^{3+}	1.55	1.49	1.45	0.97	2.15	0.24	0.49
Cl^-	141	111	97.4	51.9	296	113	106

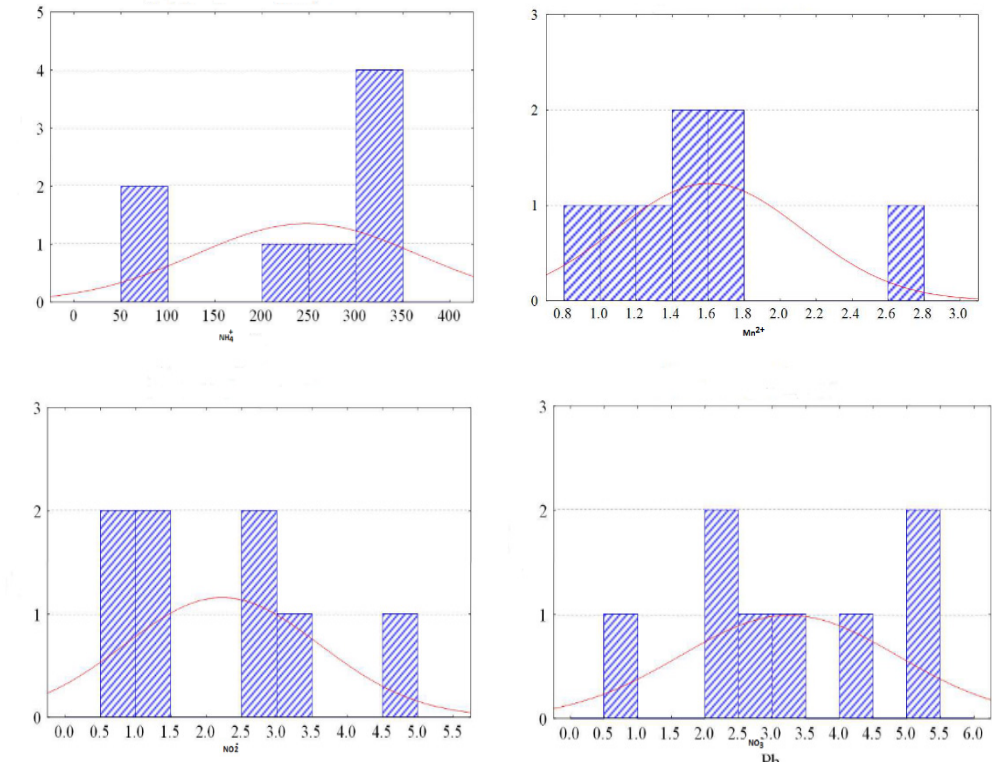

Figure 1. Frequency Histograms of some measured parameters: Mn^{2+}, NH_4^+, NO_2^-, NO_3^-

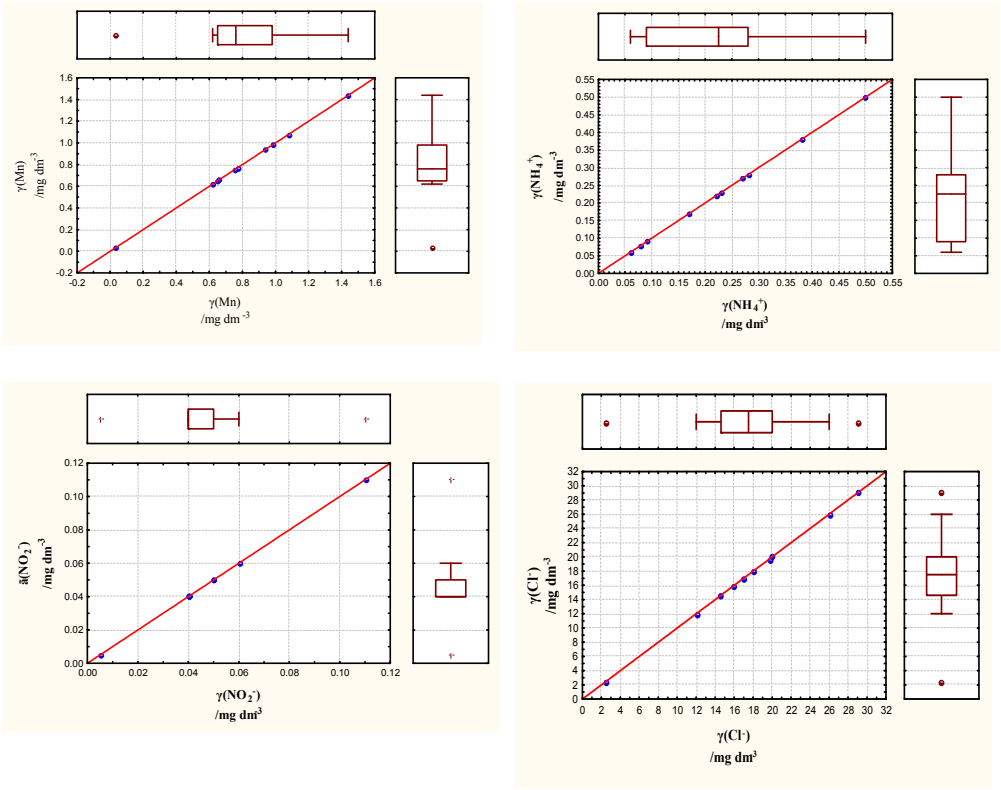

Figure 2. Two dimensional scatterplot with plots diagrams of some measured parameters: Mn, NH_4^+, NO_3^-, Cl^-

Table 3. Water samples with anomalous values (outliers and extremes) from seven variables

Sample	Outliers of elements	Extremes of elements
A_1	Cl^- (296 mg/L) Mn^{2+} (1.02 mg/L)	-
A_2	-	NO_2^--N (0.10 mg/L)
A_3	NH_3-N (0.76 mg/L)	-
A_4	-	-
A_5	Al^{3+} (2.89 mg/L) NH_3-N (0.5 mg/L)	Fe^{2+} (3.10 mg/L) NO_2^--N (0.21 mg/L) Cr^{3+} (2.15 mg/L)

Chemical data presented in the Table 1, Frequency Histograms of some measured ions (Fig.1) and Boxplot diagrams (Fig. 2), can be used for the assessment of water contamination by toxic elements according to the International permissible limits (75/440/EEC) and Kosovo National limits (UA13/2008) and EU directives.

The physic-chemical parameters such as: water temperature, pH, conductivity, total dissolved solids (TOS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), hardness, concentration of Cl^- NO_3^--N, NO_2^--N, NH_3-N, PO_4^{3-}-P, SO_4^{2-} Ca^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+} generally appeared to be significantly concentrated in the River water Sitnica, it is evident that in this River all used waters from Kosovo Power Plants (Kosovo "A" and "B'') are discharged there, and the leached waters of all ash disposals and two surface open mine (Mirash and Bardh) of these two power plants also.

Temperature varied at different locations of the river as indicated by the *in-situ* readings. It is not considered coming from heat contamination sources, but from natural warming in different parts of Kosovo. The high pH value at stations A_2 A_3 A_4 A_5 is due to the discharge of water from Thermo Power Plant Kosovo "B" after treatment with lime. Conductivity ranged from 431-584 μScm^{-1} these values were within highest desirable limit (75/440/EEC). If we compare conductivity separately, the lowest value is observed at A_2 station and the highest value is observed at A_3 station. Higher conductivity values indicate the presence of higher content of dissolved salts in the water. The values of hardness of water have described positive correlation with Mg^{2+} and Ca^{2+} concentrations. The lowest Hardness value is observed at A_1 station (4.07°dH) and the higher value of the hardness was observed at station A_5 (13.9°dH). Chemical oxygen demand (COD) and Biochemical oxygen demand (BOD) reaches maximum values at A_5 station (29.8 mg/L COD and 32 mg/L BOD).

The concentrations of chlorines were below 200 mg/L (maximum admissible concentration, according to EU Directive), except for concentration found in A1. The concentration of NO_3^--N above 10 mg/L which causes the lowest toxic effect at all locations A_1-A_5.The concentration of NO_2^--N were above 0.005 mg/L, which causes the significant effect, was found at all stations. The concentration of NH_3-N above 0.1 mg/L causing significant toxic effect were found at stations A_3 and A_5. The concentration of PO_4^{3-}-P above 0.25 mg/L, which causes the significant effect, was found at stations A_3 and A_5. The concentration of Mn above 0.05 mg/L (meaning the maximum admissible concentration, according to EU Directive) causing significant toxic effect were found at all stations A_1-A_5.The highest concentration was found at station A_1 (1.02 mg/L). Concentration of Fe above 0.3 mg/L, which causes the significant toxic effects, was found at all stations A_1-A_5. The highest concentration of Fe was found at station A_3 and A_5 (A_3: 3.02 mg/L and A_5: 3.10 mg/L). The concentrations of Al^{3+} above 0.2 mg/L which causes the toxic effects, were

found at all locations A_1- A_5. The highest concentration of Al^{3+} was found at station A_5 (2.89 mg/L), as a result of anthropogenic pollution. The concentration of Cr above 0.05 mg/L which causes the toxic effects, were found at all locations A_1-A_5. The highest concentration of Cr was found at station A_5 (2.15 mg/L), as a result of anthropogenic pollution.

The presence of toxic parameters and trace metals in the River water Sitnica in these five sample places is in fact the result of the producible activity of Kosovo power plants which use lignite as a combustible material and which after combustion releases a considerable amount of ash. Created disposals from residues after the combustion of lignite are near river Sitnica is the permanent way to indicate in the quality of its water. High concentration of chromium in these sample places can be described as a variety of agricultural and industrial activities in this region. Farmers, with their activity in agro production, use different chemical preparations, which contain chromium, and which together with raw waters from agricultural surfaces, arrive till the river Sitnica. The raw material used for the production of electricity at Kosova Thermal power plants is coal. These plants use large quantities of water and have no wastewater treatment. Working activity in these plants results in water pollution which after discharge into water causes environmental impact. Polluted water discharged from these plants into the Sitnica river results in pollution with significant impact on local and regional level.

The discharge of polluted water from coal mines, thermal power plants and existing ash landfills is a result of disregarding the environmental legislation. The obtained results from the samples taken at different locations before they discharge into the Sitnica River revealed that they are polluted in quality aspect from mines and in quantity aspect from power plants. Advanced wastewater treatments such as classification, treatment, flocculation and filtration of the discharged waters would enable their re-use and minimization the pollution of the river Sitnica which further discharged into the Iber River.

CONCLUSIONS

In order to determine the level of contamination of Sitnica river water, the following parameters: Cl^-, NO^-_3-N, NO_2^--N, NH_3-N, PO_4^{3-}-P, SO_4^{2-} and trace metals: Al^{3+}, Fe^{2+}, Cr^{3+}, Mn^{2+} concentrations were investigated in five selected sampling sites. The study revealed that the enhanced concentration of toxic parameters of Sitnica river is due to the anthropogenic influences.

International permissible limits (75/440/EEC) and Kosovo national limits (UA13/2008) were applied to assess the river water contamination. The results showed that the Sitnica River is heavily polluted, the highest concentrations were recorded in the sampling spots A_3, A_4 and A_5.

These spots correspond to the locations in Plemetin (A_3), the nearest to the Thermo Power Plant Kosovo ”B”, between the landfill coal and ash (A_4) and in the Sitnica River where the water used in Thermo Power Plant Kosovo “B’’ is discharged (A_5).

The results of this study provide the baseline data which can be used by Kosovo authorities for environmental management. It can be concluded that the input of industrial discharge of water from Thermo Power Plant Kosovo “B” into the Sitnica river is responsible for the intense contamination of the water and must be regarded as a major concern.

In order to protect the river water from further contamination, the remediation options in order to reduce the anthropogenic discharges are suggested.

EXPERIMENTAL SECTION

Sitnica River is one of the main rivers in Kosovo. The river is located in the area with high anthropogenic pressure, were the contamination of river with different pollutants presents a complex long-term environmental problem. Summers are warm and dry, while winters are cold and rainy. Annual average air temperature reaches 17.1 ºC.

Average temperature during the coldest month (January) is -2.4 ºC and 24.2 ºC during the warmest month (July). The highest rainfall is recorded between October and March 500-700 mm/year (data from the Meteorological and Hydrological service of the Republic of Kosovo), the lowest between June and August 200-300 mm/year. Precipitation varies from 600 to 1400 mm/year. It is important to evaluate how climate has varied and changed in the seasons. Climate change can directly affect the hydrological cycle and, through it, the quantity and quality of water resources.

The water samples from Sitnica River were collected from five stations every three months at monthly intervals (in triplicate) during the period from June 2015 to September 2015.These stations are covering the upstream and downstream sites of major industrial area of Obiliq city close to Thermo Power Plant (TPP) Kosovo “B” as the main power plant in the country. Geographical positions were determined by GPS, using model “Magelau”. The sampling stations are shown in Fig. 3.

Five water samples were taken from along the banks of the sampling station on summer period. Analyses of samples were done according to standards methods for surface water ISO 5667-1(2006) [5,7]. The study area with the sampling locations is shown in Fig.3 and the details about all sampling sites. Sampling tools were washed and dried with water before the next sample was collected. Water samples were collected from 10 cm below the surface water [7]. The collected samples (1dm^3) were stored in polythene plastic containers. According to the requirements samples were preserved in the refrigerator after treatment. The study area with the sampling locations is shown in Figure 3 and the details about all sampling sites are presented in Table 4.

Figure 3. Study area with sampling stations

Table 4. Sampling stations with detailed locality description

Sample	Locality	Coordinates	Height above sea level (m)
A_1	To the Thermo Power Plant Kosovo "B"	WPT=451 Y=34505450 X=4721132	541
A_2	Place where discharged water used from facilities the Thermo Power Plant Kosovo "B"	WPT=450 Y=34506102 X=4724197	534
A_3	Plemetin	WPT=448 Y=34504668 X=4726378	536
A_4	The near the Thermo Power Plant Kosovo "B" between the landfill coal and ash	WPT=449 Y=34503772 X=4726063	542
A_5	In the Sitnica River where discharged water used from TPP Kosovo "B''	WPT=447 Y=34503151 X=472840	533

*WPT-Format Waypoint

All instruments were calibrated according to manufacturer's recommendations. All tests were performed at least three times to calculate the average value. Temperature of water was measured immediately after sampling, using digital thermometer, model "Quick 63142". Measurements of pH were performed using pH/ion-meter, "Metrohm". Electric conductivity was measured by conductometer "Metrohm". Some of physic-chemical parameters (NO_2^--N, NO_3^--N, NH_3-N, PO_4^{3-}P, Al^{3+}, Mn^{2+} and Fe^{2+}) were determined using UV-VIS spectrophotometry method.

A CAMSPEC Model UV-VIS double beam spectrophotometer with a 10mm optical path cell was used for spectrophotometric measurements. Spectral range was 190-1100 nm. Its measurement region, in a cuvette of 10 mm, was λ = 340-800 nm, is dedicated for drinking waters analysis, discharged and sea water.

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