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Impact of Kishnica mines on pollution of the Graçanka River and water wells nearby, Kosovo

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Abstract

Mining is an important economic activity in Kosovo. Artana and Kishnica mines are a part of the Trepça industrial complex and the increased exploitation of deposits has resulted in undesirable impact on the environment around the mining sites. More specifically, the mining activity caused water pollution. The aim of the study was to assess the physico-chemical parameters and presence of heavy metals (Ni, Zn, As, Cd, Pb, Cr, Mn, Fe) in water samples of the Graçanka River and household wells in the area. The Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine metal concentrations. Samples were collected from five sites along the Graçanka River and from four private water wells during a period from September to November 2019. Concentrations of heavy metals in the Graçanka River were as follows Mn (24–1203 $\mu g \cdot dm^{-3}$), Fe (11–785 $\mu g \cdot dm^{-3}$), Ni (4–299 $\mu g \cdot dm^{-3}$), Pb (2–22 $\mu g \cdot dm^{-3}$), As (1–5 $\mu g \cdot dm^{-3}$), Zn (344–1646 $\mu g \cdot dm^{-3}$), Cr (1–2 $\mu g \cdot dm^{-3}$) and Cd (<1 $\mu g \cdot dm^{-3}$). The well waters were polluted by multiple metals (Mn > Fe > Ni > Pb) with concentrations of Mn 1834–36089 $\mu g \cdot dm^{-3}$, Fe 158–3535 $\mu g \cdot dm^{-3}$, Ni 82–1882 $\mu g \cdot dm^{-3}$, Pb 5–45 $\mu g \cdot dm^{-3}$, As 2–19 $\mu g \cdot dm^{-3}$, Cd 1–12 $\mu g \cdot dm^{-3}$, Zn 979–23474 $\mu g \cdot dm^{-3}$ and Cr 1–2 $\mu g \cdot dm^{-3}$. The pollution has been caused by industrial (mining-related) and urban discharges. The contamination originates from the release of flotation process waste and from the leaching of the tailings dam. Most probably, rainwater has washed contaminants into the aquifers and the Graçanka River. River water is not suitable for irrigation and well water is not suitable for consumption or irrigation. Wastewater should be treated before discharge and the tailings area should be remediated in order to stop the pollution.

Key words: *mines*, *pollution*, *the Graçanka River*, *water quality*, *water wells*

INTRODUCTION

Mining is an important industry for economic development around the world. Being a developing country, Kosovo's mining is a primary industry which was once the backbone of the economy. Today, the Trepça Industrial Complex is the leading company in the sector, which includes Kishnica and Artana mines. The two important mines, rich in Pb-Zn ores and other metals, contribute greatly to the national mineral production. Mining has a negative impact on the environment from generated wastes and pollutants. A variety of pollutants are generated by ore mining, which then diffuse into the surrounding environment and contaminate water, air and soil [LEPPÄNEN *et al.* 2017]. In mining regions, natural water composition vary in function of quantities and qualities of mining water receipted, meteoric water and residual water overflowed [BUD *et al.* 2007]. Mining by its nature consumes, diverts and can seriously pollute water resources [EMMANUEL *et al.* 2018]. There are four main types of mining impacts on water quality: acid mine drainage, heavy metal contamination and leaching, process chemicals pollution and erosion and sedimentation [EMMANUEL *et al.* 2018]. A serious water pollution from mining operations is the contamination with heavy metals, particularly copper, lead, cadmium and arsenic. Although these elements occur naturally in trace quantities in the environment, mining and smelting processes increase their "loadings" to toxic levels [HILSON 2000]. The monitoring of water quality is an important component of water management [ZHUSHI *et al.* 2020]. Therefore, the investigation of the level of contamination and impacts of the pollution on the quality of water courses is pertinent because of the critical roles played by water resources [OBETA *et al.* 2019]. Heavy metal contamination in water environments has received considerable attention worldwide due to not only toxicity but also persistence, abundance, and biomagnification in the environment and their subsequent accumulation in aquatic habitats [WEI *et al.* 2018].

Various studies have examined well water quality [BERISHA, GOESSLER 2013] and quantified metal pollution in river water in Kosovo, including the Ereniku River [MALOKU *et al.* 2015], Mirusha River [GASHI *et al.* 2017], and Trepça and Stinica Rivers, contaminated by the mining industry [FERATI *et al.* 2015].

Mining in Kishnica mines has induced negative impact on the environment by producing enormous quantities of waste (tailings dam). Flotation and municipal wastewaters are discharged to the Graçanka River and could contaminate well water in the vicinity. Water wells are important sources for drinking water in the region. The tailings dam situated in Graçanica contains toxic heavy metals such as Pb, Zn, Cd, As, Cu, Mn and Fe. Erosion and precipitation, especially during rainy season and strong wind, degrade the environment around the town and cause drastic cases of air, water and soil pollution [VITAKU *et al.* 2013]. In addition, it is necessary to mention that the acidic tailing with heavy toxic metals adversely affect regional water courses, such as the Graçanka River near the town and cross-boundary rivers and streams [VITAKU *et al.* 2013]. High concentrations of heavy metals have strong toxic effects and they constitute an important component of environmental pollution [CHEHREGANI, MALAYER 2007]. Recently, anthropogenic activities have consistently increased the quantity of heavy metals in aquatic ecosystems, so heavy metal pollution in the aquatic system is growing at an alarming rate and has become a significant problem worldwide [MALIK *et al.* 2010]. The primary focus of our study was to assess impact of the mining industry on water quality of the Graçanka River and examine well water samples using physico-chemical parameters and heavy metal concentration.

MATERIALS AND METHODS

In order to understand the spatial character and the magnitude of water quality problems in riverine and well water, we conducted an extensive well water and river water survey at the Graçanka River area. The monitoring network consisted of nine monitoring points (Fig. 1, Tab. 1). Five water samples were collected from the Graçanka River, marked as: S_1, S_2, S_3, S_4 and S_5, and four from drinking water wells, marked as: S_6, S_7, S_8 and S_9.

These samples were handled and transported for chemical analysis in accordance with paragraph 5.4 of EN ISO/IEC 17025. The water samples were transported in

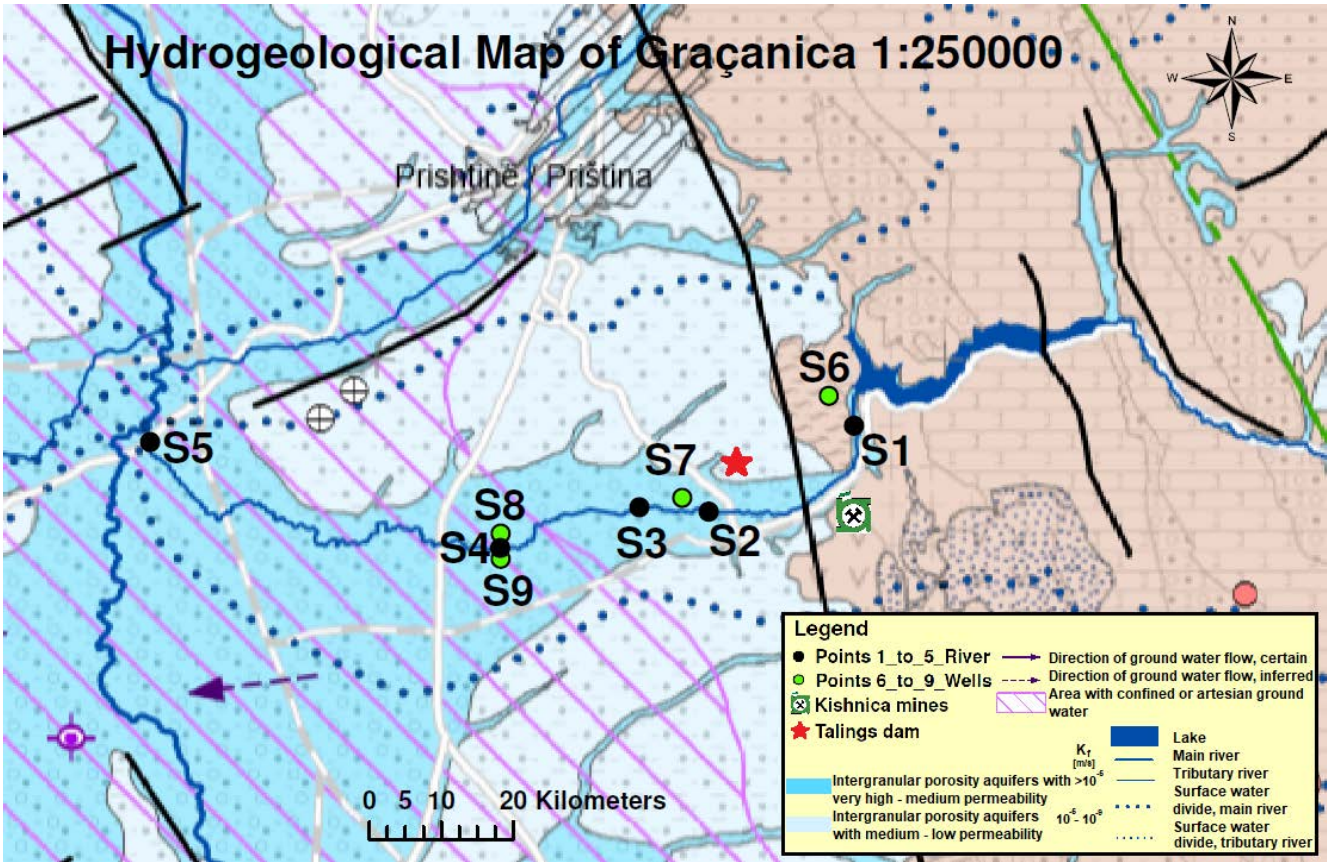

Fig. 1. Monitoring network in the municipality of Graçanica; source: own study

Table 1. Geographical coordinates of the sampling sites

Sampling site	Geographic latitude	Geographic longitude	Altitude (m a.s.l)	Distance (km)
S1	42°36'34.88"	21°13'10.53”	610	0.8
S2	42°35'59.73”	21°11'59.79”	590	1.5
S3	42°36'0.72”	21°10'54.47”	583	3
S4	42°35'40.41”	21°8'49.98”	564	6
S5	42°36'40.21”	21°4'2.36”	538	13
S6	42°37'4.11”	21°13'5.35”	620	1.5
S7	42°36'1.26”	21°11'38.96”	587	2
S8	42°35'43.20”	21°8'52.39”	566	6
S9	42°35'36.08”	21°8'48.25”	566	7

Explanations: S1–S9 = sampling points as in Figure 1.
Source: own elaboration.

glass or polyethylene bottles, cleaned with hydrochloric acid and rinsed with distilled water, and finally closed with a stopper. The volume of a sample was 1 dm^3 and the preservation was conducted in accordance with the conservation procedure of American Public Health Association [EATON *et al.* (eds.) 2005].

With the use of relevant methods, water samples were tested to determine pH, turbidity, electrical conductivity (*EC*), total dissolved solids (TDS), dissolved oxygen (DO), oxygen saturation, total suspended solids (TSS), chemical oxygen demand (*COD*), biochemical oxygen demand (BOD_5), total organic carbon (TOC), detergents, ammonia (NH_4-N), nitrites (NO_2^-), nitrates (NO_3^-), phosphates (PO_4-P), inorganic nitrogen, organic nitrogen, total nitrogen (TN), total phosphorus (TP), chlorides, and sulphates.

Preparation of water samples for the heavy metal concentration analysis was based on mineralization of samples using EPA 3015A method [EPA 2007]. The content of arsenic (As), zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni), chrome (Cr), manganese (Mn), iron (Fe) has been determined in water samples using the ICP-MS in the IHMK environmental analysis laboratory. Heavy metals were measured in their ionic concentrations.

Assessment of river water quality was based on ISO 5667-6 for surface water and ISO 5667-11 for groundwater.

Minitab 18 was used for the statistical data analysis – principle component analysis (PCA). Raw data were used for the PCA using a correlation matrix.

RESULTS AND DISCUSSION

Physico-chemical parameters and the concentration of heavy metals were assessed in water samples from the Graçanka River and water wells, collected from September to November 2019. Results were calculated as mean values for September–October and November.

Results were compared with reference values for the maximum allowable limit (MAL) provided by Administrative Instruction No 16/2012 of the Republic of Kosovo for the quality of water for human consumption, and Administrative Instruction MESP-No 16/2017 on the classification of surface water bodies.

EVALUATION OF ECOLOGICAL STATUS AND HEAVY METAL POLLUTION OF THE GRAÇANKA RIVER

Physico-chemical parameters (pH, DO, BOD_5, *COD*, NH_4-N, NO_3, TN, PO_4-P, TP) were used to assess the ecological status of the river water. These parameters were compared with reference values (MAL – maximum allowable limit) of the AI 16/2017 as shown in Table 2. The final classification indicates that the Graçanka River water samples have poor (P) ecological status, the lowest in this classification.

Concentrations of heavy metals at each site are given in Figure 2, and their respective ranges are as follows: Mn (24–1203 $\mu g \cdot dm^{-3}$), Fe (11–785 $\mu g \cdot dm^{-3}$), Ni (4–299 $\mu g \cdot dm^{-3}$), Pb (2–22 $\mu g \cdot dm^{-3}$), As (1–5 $\mu g \cdot dm^{-3}$), Zn (344–1646 $\mu g \cdot dm^{-3}$), Cr (1–2 $\mu g \cdot dm^{-3}$) and Cd (<1 $\mu g \cdot dm^{-3}$).

MALs for heavy metal concentration were exceeded in the water samples from the Graçanka River. Two heavy metals (Ni and Zn) exceeded the standards almost in all sites, while six heavy metals (As, Cd, Pb, Cr, Mn, Fe) were within the standards. The MAL for Zn was exceeded in five sites with the highest concentration of 1646 $\mu g \cdot dm^{-3}$ detected at site S4. The MAL for Ni was exceeded at three sites (S2, S4 and S5), with the highest concentration of 299 $\mu g \cdot dm^{-3}$ at site S4. Therefore, we can conclude that water pollution in the Graçanka River is the result of intensive exploitation of Kishnica mines (flotation process) and urban discharges.

EVALUATION OF WELL WATER PHYSICO-CHEMICAL PARAMETERS

MALs were exceeded for some physico-chemical parameters in well water. Turbidity, total suspended solids (TSS), nitrite and sulphate were above MALs at site S6, ammonia and nitrates at site S7. Sites S8 and S9 had ammonia values beyond MAL. In potable water, concentrations of nitrite and nitrate above MALs are a public health concern. Such high levels of nitrate and nitrite can cause methemoglobinemia, blue baby syndrome [GUPTA *et al.* 2000] which are associated with a thyroid dysfunction in

Table 2. Comparison of parameters and assessment of the Graçanka River ecological status

Sampling site	pH	DO	BOD_5	*COD*	NH_4-N	NO_3	TN	PO_4-P	TP	Final classification
S1	7.24	8.00	4.8	9.2	0.573	0	0.833	0.010	0.261	P
S2	6.82	6.27	4.8	11.6	1.329	0.1	1.451	0.070	0.348	P
S3	7.16	3.95	61.0	113.0	4.253	0.1	7.131	1.876	3.776	P
S4	7.07	4.19	46.8	105.1	4.983	0.1	7.369	1.787	3.525	P
S5	8.16	7.00	33.6	46.7	6.531	2.6	7.346	1.623	1.837	P

Explanations: status: DO = dissolved oxygen, BOD_5 = five-day biological oxygen demand, COD = chemical demand, TN = total nitrogen, TP = total phosphorus; G = good (green), Md = moderate (yellow); P = poor (red).
Source: own study.

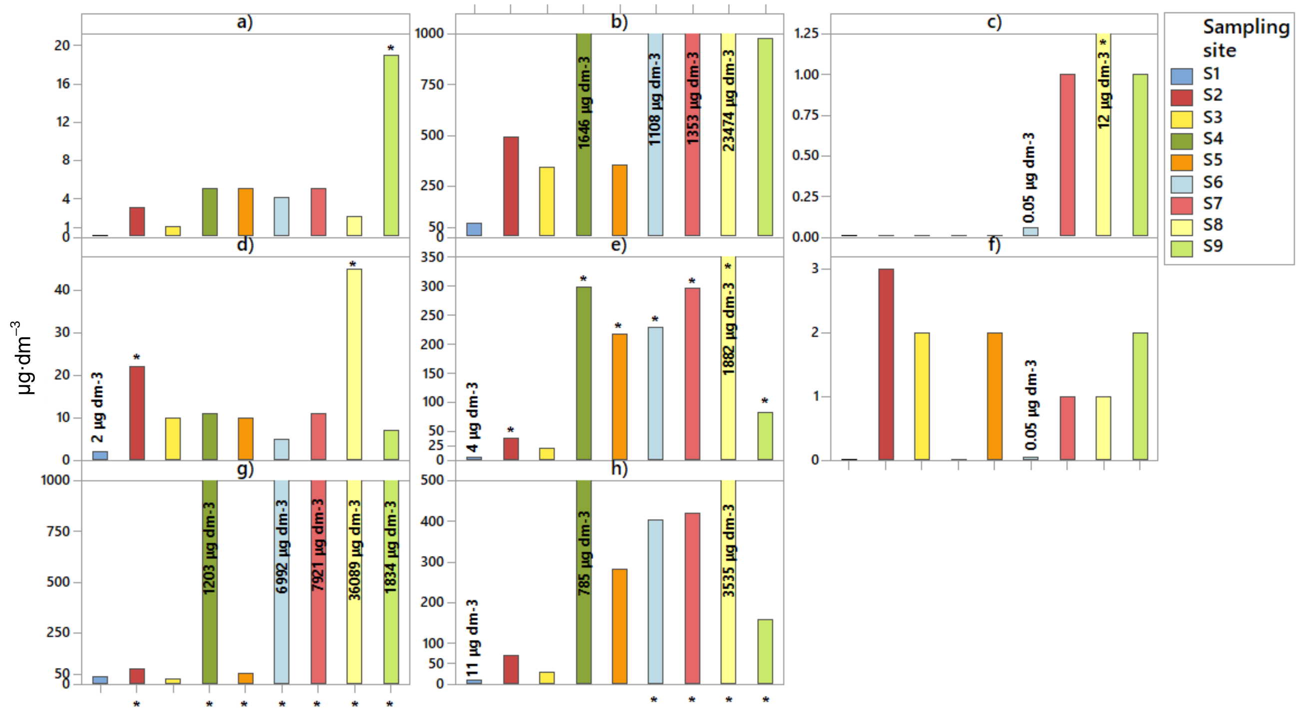

Fig. 2. Heavy metal concentrations in water samples (S1–S9); a) As, b) Zn, c) Cd, d) Pb, e) Ni, f) Cr, g) Mn, h) Fe; S1–S9 as in Fig. 1; * – exceeds national limit (MALs AI); bar chart cut-off – for values that do not fit the figure; source: own study

children [GATSEVA, ARGIROVA 2008; TAJTAKOVA *et al.* 2006] and in pregnant women [GATSEVA, ARGIROVA 2008].

EVALUATION OF WELL WATER HEAVY METAL POLLUTION

Heavy metal concentrations exhibited high variation (Mn 1834–36 089 μg·dm^{-3}, Fe 158–3535 μg·dm^{-3}, Ni 82–1882 μg·dm^{-3}, Pb 5–45 μg·dm^{-3}, As 2–19 μg·dm^{-3}, Cd 1–12 μg·dm^{-3}, Zn 979–23474 μg·dm^{-3} and Cr 1–2 μg·dm^{-3}). Heavy metal concentrations for Mn, Fe, Ni, Pb, As and Cd exceeded MALs in multiple well sites, whereas Zn and Cr were within standards. Mn concentrations in well water were at dangerous levels. The reducing condition of groundwater and some lakes and reservoirs support high manganese levels; concentrations up to 1300 μg·dm^{-3} in neutral groundwater and 9600 μg·dm^{-3} in acidic groundwater have been reported [WHO 2011]. Average concentrations of heavy metals in well water were found in the following order Mn > Fe > Ni > Pb > As > Cd > Zn > Cr. Flotation wastewater is discharged to the Graçanka River which can indirectly affect well water and water aquifers situated beneath the tailings dam (Fig. 1). Pollution via groundwater may have reached water wells that are far away and caused water contamination. So, as regards well water used for drinking purposes, analyses have shown not only the presence of heavy metals but their concentrations exceeded MALs at all sampling sites (S6–S9). Well water is unsuitable for drinking and irrigation. Luckily, these wells are not used for abstracting drinking water due to warnings issued by authorities.

PRINCIPLE COMPONENT ANALYSIS

Variations among the samples for physico-chemical properties are shown in the PCA biplot (Fig. 3). Sites S1, S2, S6, S7, S8 and S9 plot to left hand side of the biplot, S5 to the right side of the biplot, whereas S3 and S4 are more scattered. Sites S3 and S4 are characterized by high concentrations of various parameters due to close proximity of the tailings dam, whereas S1 and S2 exhibit high concentrations of nitrite and dissolved oxygen, which shows that water flow velocity reduces the impact of tailing dams.

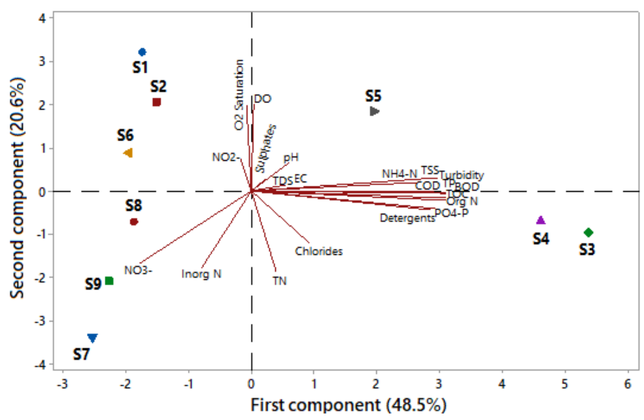

Fig. 3. Principle component analysis biplot for physico-chemical parameters (S1–S9); S1–S9 as in Fig. 1; source: own study

As regards well sites, biplot results are more clear. Sites S7, S8 and S9 are characterized by high concentrations of nitrate and inorganic N, which suggests the impact of municipal wastewater discharge.

Variations among the samples for heavy metals are shown in PCA biplot (Fig. 4). Sites S1, S2, S3 and S5 plot to left hand side of the biplot, S4, S6 and S7 to the right and side of the biplot, whereas S9 is more scattered. Site S4 is characterized by high concentrations of Zn, Mn, Ni, and Fe due to close proximity of the tailings dam. Site S2 appears to be polluted by Cr and Pb.

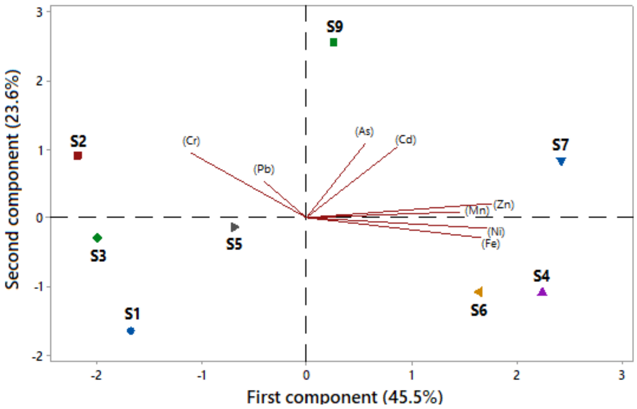

Fig. 4. Principle component analysis biplot for heavy metal concentrations (S1—S7, S9); S1–S7, S9 as in Fig. 1; source: own study

For well sites, the biplot results are less clear. Site S7 is characterized by high concentrations of Zn, Mn, Ni, and Fe and site S9 exhibit high concentrations for As and Cd, which suggests the impact of the tailings dam and municipal wastewater discharge on groundwater aquifers. Heavy metal contamination of aquifers has caused well water pollution and extremely high concentrations at site S8 which was not subject to the PCA due to its preeminence. However, site S6 located upstream from the mine site has shown more complex groundwater movement than previously thought. This is another issue which should be urgently studied in detail.

CONCLUSIONS

Intensive exploitation of the Kishnica mines, tailings dam and urban discharges have caused not only environmental degradation but they also polluted the Graçanka River and water wells in the vicinity. Graçanka is one of rivers with the poorest ecological status. Well water is contaminated with heavy metals. River water is not suitable for irrigation, whereas well water is neither potable nor suitable for irrigation. Wastewater treatment prior to its discharge is a must for the mining industry and the same applies to the remediation of the tailings dam. Therefore, the Ministry of Environment and Spatial Planning of Kosovo needs to take preventive measures to eliminate pollution sources in order to convert the Graçanka River water into an important positive component of the aquatic ecosystem.

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